Plasmonic Hot Carrier Transfer Modulated Room−Temperature Visible Light Emission of Cu₂O−Au Nanowires

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Abstract. Cu₂O nanowires decorated with Au nanoparticles (Cu₂O−Au NWs) were synthesized by a facile solution method. Due to light excited plasmonic hot carrier transfer from Au nanoparticles into Cu₂O nanowires, under 360 and 420 nm light excitation, the fluorescence emissions of Cu₂O−Au NWs, compared with that of Cu₂O nanowires, were enhanced 4.03 and 3.35 times, respectively. The decay time of Cu₂O−Au NWs is 4.85 times longer than that of Cu₂O NWs under 337 nm light excitation. The results indicate that hot carrier transfer can effectively modulate the optical properties of Cu₂O NWs.

1. Introduction

As an attractive p−type direct bandgap oxide semiconductor, cuprous oxide (Cu₂O) nanostructures have attracted more attention in photodetection, photoelectrochemistry and solar cells etc., due to the high carrier mobility (up to 10² cm/(V.s)), good optical absorption, low cost, and non−toxicity [1−4]. Recently, numerous Cu₂O nanostructures with good morphology and crystallinity have been reported, such as nanocages, nanocubes, and nanowires [5−7]. Among these nanostructures, Cu₂O nanowires (NWs) have received particularly concern owing to their efficient transport of carriers within small dimension and intrinsical anisotropy [8].

In Cu₂O NWs−based optoelectronic devices, the demand of higher performance not only requires the simple engineering of their energy bandgap, but also requires further modulation of their properties, such as photoluminescence (PL) emission and decay properties. It has been reported that the integration of semiconductors and noble metals (such as Au) nanoparticles (NPs) can effectively modulate the optical properties of semiconductor [9]. Metal NPs are stimulated by incident light to induce local surface plasmon (LSP). LSP can excite hot carriers through non−radiative decay. These hot carriers are transferred to adjacent semiconductor, and can significantly affect the optical and electrical properties of semiconductor [10]. Therefore, it is valuable to study the influence of hot carriers on the fluorescence emission and decay properties for the application Cu₂O−Au NWs based optoelectronic devices. However, as far as we know, the influence of hot carrier transfer on the PL properties of Cu₂O−noble metal heterostructures is rarely reported, and there are still a lot of work to be done.

In this work, Au NPs decorated Cu₂O (Cu₂O−Au) NWs were synthesized by a facile solution method. For Cu₂O−Au NWs, modulation of optical properties by hot carrier transfer was studied by PL investigation. Compared with individual Cu₂O NWs, the PL emission of Cu₂O−Au NWs at 430 nm was enhanced 4.03 times under 360 nm excitation, and the PL emission was enhanced 3.35 times under 420 nm excitation. Under 337 nm excitation, the PL decay time of Cu₂O−Au NWs was...
enhanced 4.85 times. Cu$_2$O–Au NWs have great potential in optoelectronics based on plasmonic hot carrier transfer.

2. Experiments
The Cu$_2$O NWs were prepared by a previously reported method with a minor revision [7]. In brief, a mixture of 10 mL 0.10 M pyrrole aqueous solution and 40 mL 0.0206 mM copper acetate solution was stirred until the mixture turned olive green. Afterward, the mixture was injected into autoclave, maintained at 180 °C for 10 hours. As the temperature decreased to room temperature, the sediment (Cu$_2$O NWs) was centrifuged.

After that, HAuCl$_4$ solution (10 mL, 1 mM) and 1M NaOH solution was mixed until the pH = 8. After 0.1 g ascorbic acid and 0.0318 g polyvinylpyrrolidone were completely dissolved in 10 mL distilled at 90 °C, the as-synthesized Cu$_2$O NWs were dropped into the solution. Next, the 5 mL of as-prepared HAuCl$_4$ solution was dropped into the solution. 1.5 hours later, another 5 mL HAuCl$_4$ solution was injected. Finally, the Cu$_2$O–Au NWs were separated by centrifugation.

In the PL experiments of Cu$_2$O NWs and Cu$_2$O–Au NWs, we guarantee that the concentrations of Cu$_2$O NWs and Cu$_2$O–Au NWs are equal by strictly equivalent operation. The details are as follows: Firstly, the as-prepared Cu$_2$O NWs ethanol solution was divided equally into two parts. One was used for the synthesis of Cu$_2$O–Au NWs. Secondly, the Cu$_2$O–Au NWs and Cu$_2$O NWs were centrifuged under the same conditions. Finally, Cu$_2$O–Au NWs and Cu$_2$O NWs were dispersed equivalently in 5 mL ethanol solution, respectively.

The crystal structures of samples were analyzed by using BRUKER D8–ADVANCE X–ray diffractometer. The microstructure and morphology of the samples were characterized by using transmission electron microscopy (FEI Tecnai G2 F30 S–Twin) and scanning electron Microscope (JEOL JSM–7001F). Photoluminescence (PL) and fluorescent decay time were measured by fluorescence spectrophotometer (Quanta Master™ 40). All PL measurements were tested in ambient environment (atmospheric environment, 25 °C, relative humidity 60%).

3. Results and Discussion

![Figure 1](image)

**Figure 1.** a, XRD pattern of Cu$_2$O–Au NWs, Cu$_2$O NWs, and Au NPs. b, c, SEM images of Cu$_2$O NWs. d, SEM image of Cu$_2$O–Au NWs. e, SEM image of single Cu$_2$O–Au NW. f, TEM images of a Cu$_2$O–Au NW.
X-ray diffraction (XRD) pattern shows that diffraction peaks of Cu₂O NWs and Au NPs are consistent with simple cubic Cu₂O (JCPDS card no. 05−0667) [11], and face center cubic Au (JCPDS card no. 4−784) [12], respectively (Fig. 1a). The scanning electron microscope (SEM) images show the Cu₂O NWs are gracile (average diameter is ~ 172 nm, length is ~ 10−90 µm) and smooth (average surface roughness is ~ 0.00169) (Fig. 1b, c). SEM images reveal that average diameter of Au NPs is ~ 50 nm and area density of Au NPs on a Cu₂O NW is > 35/µm² (Fig. 1d, e). Transmission electron microscopy (TEM) image indicate that Au NPs are directly attached to Cu₂O NW, which is contribute to the hot carriers transfer (Fig. 1f). It is noted that a thin layer on Cu₂O NW sidewall derives from small amount residues of pyrrole and corresponding oxide.

![Figure 2](image_url)

**Figure 2.** a, PL excitation spectra of Cu₂O NWs and Cu₂O−Au NWs monitored at 548 nm emission. b, c, PL emission spectra of Cu₂O NWs and Cu₂O−Au NWs under 360 nm and 420 nm excitation, respectively.

PL is a nondestructive technique, which can be used to investigate optical properties of NW and further explore hot carrier transfer in nanostructures [13]. Fig. 2a is the PL excitation spectra of Cu₂O NWs and Cu₂O−Au NWs (emission wavelength of 548 nm). They have strong absorption in 300−500 nm, and two sharp peaks at 420 and 470 nm. The peak at 420 nm originates from transition from Γ⁸⁺ in Cu₂O valence band to Γ₂− in conduction band [14]. The peak at 470 nm is attributed to transition from Cu d−shell in valence band to sub−levels in conduction band [8]. Cu₂O NWs have four key PL emission peaks at 452, 469, 493 and 548 nm (Fig. 2b). The emission peak at 548 nm (2.26 eV) approaches the previously reported bandgap energy of Cu₂O at the Γ point (E₀B, 2.304 eV) [15], so it can be considered as near−band edge emission of Cu₂O NWs. The emission peak at 493 nm can be attributed to band edge emission of Cu₂O NWs. The emission peaks (452 nm and 469 nm) originate from excitonic transitions from different sublevels in conduction band to Cu d−shells in valence band [8].

Cu₂O−Au NWs exhibit a broadband luminescence peaked at 430 nm (2.88 eV), which can be attributed to the transition form higher sub−level in conduction band of Cu₂O to Cu−shell in the valence band [8]. PL emission of Cu₂O−Au NWs is enhanced 4.03 times compared with that of Cu₂O NWs (at emission wavelength of 430 nm). PL emission spectra of Cu₂O NWs and Cu₂O−Au NWs are almost identical under 420 nm light excitation. However, the emission intensity of Cu₂O−Au NWs is 3.35 times larger than that of Cu₂O NWs (at emission peak of 548 nm, Fig. 2c). Notably, same concentration of Cu₂O NWs and Cu₂O−Au NWs can be ensured through careful treatment of experimental details in order to compare the PL intensity of Cu₂O NWs and Cu₂O−Au NWs.

In order to further verify the influence of hot carriers transfer in Cu₂O−Au NWs, Fig. 3a presents the room temperature PL decay curves of Cu₂O NWs and Cu₂O−Au NWs with a 337 nm light excitation. The PL decay curves were fitted by double exponential function [16]:

\[
I(t) = I_0 + A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right)
\] (1)

Where I(t) is PL intensity at time t, I₀ is initial luminescence intensity, A₁ and A₂ are constants, and \(\tau_1\) (\(\tau_2\)) is rapid (slow) time for exponential components. The average decay time \(\tau\) can be calculated by the following equation [16]:

\[
\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}
\] (2)
The decay time of Cu$_2$O–Au NWs (4.35 ns) is 4.85 times longer than that of Cu$_2$O NWs (0.896 ns). This shows that hot carrier transfer from Au NPs to Cu$_2$O NWs can obviously increase the PL decay time of Cu$_2$O NWs.

**Figure 3.** a, PL decay curves of Cu$_2$O NWs and Cu$_2$O–Au NWs. b, Schematic band diagram and hot carrier transfer mechanism of Cu$_2$O–Au NWs.

The enhancement of fluorescence emission and decay time of Cu$_2$O–Au nanowires can be explained by plasmonic hot hole transfer from Au NPs to Cu$_2$O NWs, as shown in Fig. 3b. In thermal equilibrium, built-in electric field causes Cu$_2$O energy band near the interface to bend downward. Under illumination, the incident light interacting with the Au NPs results into LSP and the non-radioactive decay of plasmons could inject hot carriers or resonantly excited excitons in the vicinity of the interface between the Au NPs and Cu$_2$O NWs [17]. Due to the unique electronic structure of Au (high-density electronic d-band state), when incident photon energy is larger than interband threshold (d to sp band transition, $E_{int} = 2.3$ eV), hot holes are much “hotter” (far away from Au Fermi level) than hot electrons are generated below Fermi level in Au d–band [18, 19]. Therefore, from the viewpoint of hot hole transfer, it is better to combine Au NPs with p–type Cu$_2$O NWs than n–type semiconductors, and the Schottky barrier between Au NPs and Cu$_2$O NWs is also suitable for hot hole transfer. Hot holes with energy greater than Schottky barrier height ($\Phi_B \approx 1$ eV) can be transferred across barrier to Cu$_2$O NWs, resulting in enhanced fluorescence emission and decay time of Cu$_2$O NWs.

4. **Conclusion**

To summarize, Cu$_2$O–Au NWs have been successfully synthesized by a simple solution method. Due to the light excited plasmonic hot carrier transfer from Au NPs into Cu$_2$O NWs, under 360 nm light excitation, the PL emission intensity of Cu$_2$O–Au NWs is 4.03 times larger than that of Cu$_2$O NWs at 430 nm. Under 420 nm light excitation, PL emission intensity of Cu$_2$O–Au NWs is 3.35 times larger than that of Cu$_2$O NWs. Under 337 nm excitation, the decay time of Cu$_2$O–Au NWs is 4.85 times larger than that of Cu$_2$O NWs. Cu$_2$O–Au NWs have great potential for cost-effective optoelectronics devices based on hot carrier harvesting.

5. **Acknowledgments**

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6. **References**

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