Controllable exciton bleaching and recovery observed in ZnO–Ag hybrid nanometre-sized particles

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Damping of the exciton absorption band of deaerated ZnO sol is directly related to the amount of silver photochemically deposited on the ZnO surface; recovery of this exciton band is achieved after the solution is exposed to air and silver oxide is formed.

Nanometre-sized semiconductors are a new class of materials that show third-order optical non-linearity originating from a transient change in the absorption spectrum (and refractive index) upon illumination. The strength of non-linearity is strongly dependent on the properties of the exciton band.[1] After absorption of light the binding energy and oscillator strength of the exciton generated in nanometre-sized particles is increased relative to bulk materials due to the enhanced spatial overlap between the electron and hole wave function and the enhanced coherent motion of the exciton.[2] More importantly, this bound exciton is trapped rapidly by surface defects within subpicoseconds, forming a trapped electron–hole pair.[3–5] Therefore, the surface structure plays a key role in the control of the exciton absorption band of semiconductor nanoparticles, and thus of their non-linear optical properties. Several surface modification methods, including the use of ammonia,[5] hydroxide ions,[6] amines[7] and ZnS[8] have been developed, but no direct evidence concerning the relation between the strength of the exciton absorption band and the amount of modifier has been reported. Here a new method, that shows the exciton strength of semiconductor nanoparticles can be controlled through deposition of silver, is presented.

ZnO colloids (particle diameter 3.85 ± 1.01 nm; determined by TEM measurements) were prepared in ethanol by mixing $Zn(NO_3)_2$ with NaOH in the presence of poly(vinylpyrrolidone) (PVP, M = 10 000). The final composition was 1×10^{-3} mol dm^{-3} ZnO–5×10^{-4} mol dm^{-3} OH^-–5×10^{-4} mol dm^{-3} PVP. The deposition of silver on the ZnO surface was achieved by a photochemical method: the solution containing Ag^+ and the ZnO sol was first deaerated with argon for 10 min, then exposed to UV irradiation (150 W Xe lamp, filtered with a 3 cm water filter) of intensity 1.4 mW cm^{-2} (HP 8330A radiant flux meter). The absorption (PE Lambda 2) and fluorescence (Perkin Elmer) spectra of the samples were recorded 2 min after UV irradiation in order to avoid bleaching of the aborption spectrum caused by the accumulation of electrons trapped by intrinsic defects of the ZnO particles.[9,10] No apparent change in the absorption spectra of ZnO was observed using this irradiation intensity.

OH^--covered ZnO colloids possess a distinct exciton band near 330 nm before and after mixing with $AgNO_3$ solution (Fig. 1). In the later case, it is expected that AgOH is formed on the ZnO surface [eqn. (1)].

$$Ag^+ + OH^- \longrightarrow AgOH \qquad (1)$$

After UV irradiation for 20 s a new absorption band with λ_{max} *ca.* 433 nm appeared, indicating the formation of Ag_2O [eqn. (2)].

$$2\,AgOH \xrightarrow{hv} Ag_2O + H_2O \qquad (2)$$

As irradiation proceeds this band shifted continuously to shorter wavelengths due to the continuous generation of silver on the ZnO surface (Scheme 1) which can be correlated to surface effects resulting from metal–semiconductor interactions.[11,12] Interestingly the λ_{max} values of this absorption band occurred in two ranges at different reaction times: at 433–417 nm (range 1) in the initial 4 min of reaction, where no shape change of the exciton absorption band of ZnO was observed. While upon extended irradiation, absorption occurred in the range 399–392 nm (range 2), where damping of the exciton absorption band of ZnO occurred.

Ag_2O is predominantly formed on the ZnO surface during the first 4 min of irradiation. Later, it is largely converted to silver and the corresponding absorption band is shifted to range 2. At this time, the more intensive the silver plasmon band is, the more severely damped is the exciton band of ZnO. This is ascribed to the fact that silver can act as a deep trap for electrons from the conduction band of ZnO, resulting in the damping of the exciton band of ZnO. Apparently, the extent of exciton damping can be controlled by the amount of silver deposited during UV irradiation. Similar phenomena were also observed in solution keeping [ZnO] constant but varying [Ag^+] (5×10^{-5} or 8.35×10^{-5} mol dm^{-3}).

The above assignment of the state of silver can be further illustrated in the experiments shown in Fig. 2. Upon exposure of the anaerobic ZnO–Ag colloids [Fig. 2(*b*)] to air, λ_{max} of the silver plasmon band shifted from range 2 to range 1 [Fig. 2(*c*)] and the exciton absorption band of ZnO recovered in intensity.

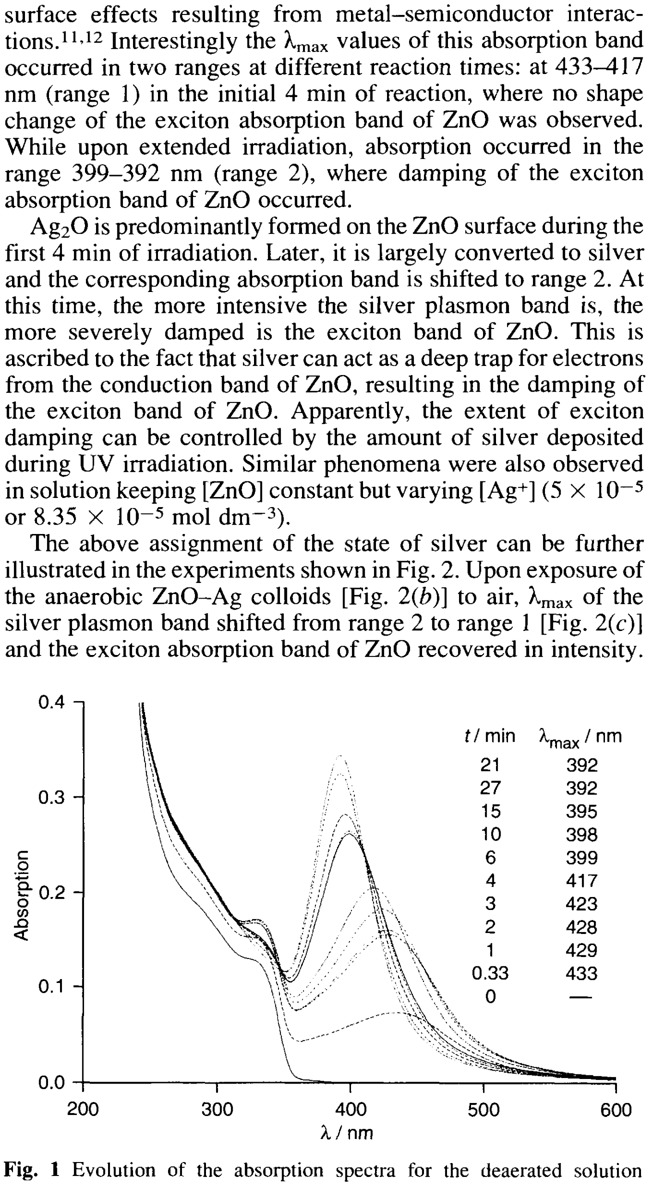

Fig. 1 Evolution of the absorption spectra for the deaerated solution containing ZnO (1.67×10^{-4} mol dm^{-3}), OH^- (8.35×10^{-5} mol dm^{-3}) and Ag^+ (1.67×10^{-5} mol dm^{-3}) during irradiation; λ_{max} corresponds to the peak wavelength of the silver plasmon band; *t* corresponds to the irradiation time

$$ZnO \xrightarrow{hv} Zn^+ + O^-$$

$$Ag_2O + Zn^+ \longrightarrow 2\,Ag + ZnO$$

Scheme 1

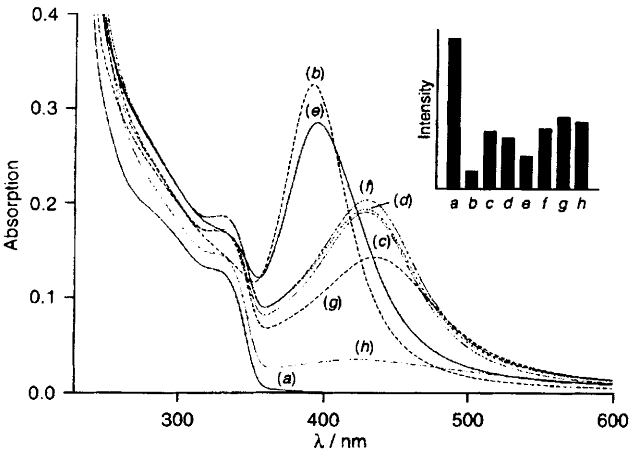

Fig. 2 Absorption spectra for solution of Fig. 1: (*a*) before irradiation; (*b*) after 27 min of irradiation (λ_{max} = 392 nm); (*c*) solution (*b*) upon exposure to air for 1.5 h (λ_{max} = 429 nm); (*d*) solution (*c*) deaerated for 10 min with argon; (*e*) irradiation of solution (*d*) for 5 min, (λ_{max} = 395 nm); (*f*) solution (*e*) upon exposure to air for 2.5 h (λ_{max} = 429 nm); (*g*) irradiation of solution (*e*) for 5 min (λ_{max} = 434 nm); (*h*) solution (*g*) upon standing for 2 min. Insert shows the visible fluorescence intensity of ZnO under the above conditions. The excitation wavelength is 330 nm.

This means that the silver formed on the ZnO surface is very reactive and is easily oxidized by oxygen [eqn. (3)].

$$2\,\mathrm{Ag} + 1/2\,\mathrm{O_2} \rightarrow \mathrm{Ag_2O} \qquad (3)$$

The silver plasmon band in range 2 can be reobtained if the above solution is deaerated and reirradiated [Fig. 2(*d*)–(*f*)]. However, if oxygen is present, the band in range 1 disappears [Fig. 2(*g*), (*h*)]. As silver is deposited on the surface of ZnO, the fluorescence intensity of ZnO decreases [Fig. 2 (insert), (*a*) → (*b*) and (*d*) → (*e*)], indicating that silver acts as a fluorescence quencher and deeply traps the photoinduced electrons. It has been reported that a trapped electron is more efficient than a trapped hole in bleaching the exciton absorption band of CdS[13] and that loading of a metal on a semiconductor surface is favourable for electron accumulation.[14]

Assuming a mean particle diameter of 3.85 nm and a density of bulk ZnO of 5.5 g cm^{-3}, then if silver is reduced on the surface of ZnO and single atom layer deposition occurs then the extent of coverage of silver on ZnO is calculated to be 10% for the solution with the composition used in the experiment (Fig. 1). Therefore, the physically most probable state of the silver on ZnO surface will be that silver clusters are evenly spread as illustrated in Fig. 3.

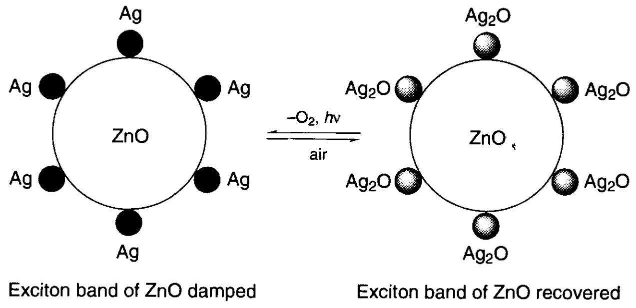

Fig. 3 Schematic illustration of the conversion of silver clusters formed on the ZnO surface and the corresponding change of the exciton band

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