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Synthesis and characterization of Ag@polycarbazole nanoparticles and their novel optical behavior

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Abstract Ag@polycarbazole as a new 3D nanocomposite material was successfully fabricated using microwave polyol reduction method followed by cations assisted oxidative polymerization of carbazole. The material was characterized by transmission electron microscopes (TEM), scanning electron microscope (SEM), FT-IR, and Raman measurements. The results confirmed that Ag nanoparticles are entirely enclosed by 3,6 polycarbazole. The interfacial study was carried out by X-ray photoelectron spectroscopy, which revealed that Ag surface atoms are intact chemically and blue shifted due to polymer composite formation. The surface plasmon resonance (SPR) and photoluminescence (PL) behavior were found quite sensitive to surface composition of Ag nanoparticles, which is greatly influenced by cations dopant and enclosing polymer in contrary way. The polycarbazole played a contributive role to counterbalance the effect of cations dopant in SPR and PL behaviors along with displaying its luminescence in violet region.

Introduction

The synthesis of 3D Ag nanoparticles and their polymer composite has great contribution in present era to produce novel materials having unit applications to fabricate nanodevices for electrical [1], optical, magnetic, catalysis, and sensing purposes [2]. These materials combine the advantageous roles of each component and display synergistic properties between polymer and metal nanoparticles [3, 4]. Moreover, the encapsulation of nanoparticles by polymer is required to prevent the nanoparticles' oxidation and coalescence [5, 6] and to sufficiently stabilize them because the materials in nanodimension are less stable and can easily loose their properties [7]. Therefore, due to the great importance of the Ag–polymer composite, the preparation of different types of Ag@polymer nanocomposites is continuously expanding.

Since last decade, Ag was encapsulated by many types of polymers, like poly(vinylalcohol) [8], poly(vinylpyrolidone), poly(methyl methacrylate) [9], and poly(vinylacetate) [10]. It was further extended for conductive polymers in order to study the electrochemical and optochemical behavior of composite materials and thus Ag-polyaniline [11], Ag-polythiophene [12], and Ag-polypyrrole [13, 14] nano-composites were prepared. All these studies were also aimed to fabricate thermally and environmentally stable product and to avoid surface touch within metal NPs, which can lead to coalescence that is not desired for functional unit's behavior of nanomaterials in nanodevices [7]. Under the same objectives, our group selected polycarbazole (PCz) as a thin coating material because, it is thermally and environmentally more stable than polypyrrole (ppy), poly (thiophene), and polyaniline (PANI) [15] and can also form coherent film on suitable substrate [16], so it is more useful to reduce the probability of surface touch within metal nanoparticles. The further interest in PCz is due to its photoconductivity, electrochromic, electroluminescence [17], photoluminescence [18], and electron–hole transporting properties [19]; hence its composite formation with Ag NPs would be prolific due to these properties.

Therefore, considering these advantageous roles of PCz, it was first time tailored around 3D Ag nanoparticles (NPs)

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by our group and successfully prepared Ag@polycarbzole as a new nanocomposite material, which showed novel optical behavior with reference to surface Plasmon resonance (SPR) and photoluminescence (PL). Herein, silver nitrate ($AgNO_3$) was reduced by microwave polyol reduction method [20] using polyvinylpyrrolidone (PVP) as templating agent, then PCz sheath was exploited around the entire surface of these Ag NPs by oxidative polymerization of carbazole using $Cu(CH_3COO^-)_2$ as an oxidizing agent in acetonitrile. During the whole course water was avoided to prevent unwanted oxidation of Ag NPs and to accomplish high solubility of carbazole for viable polymer growth. In this way Ag@PCz 3D nanoparticles were fabricated and confirmed by TEM, SEM, FT-IR, and Raman measurements. The interface was studied by XPS and the novel optical behavior of nanocomposites was studied by UV–Vis and PL spectrophotometer. The UV–Vis and PL measurements displayed pronounced effect of Cu^{2+} cations from oxidizing agent and polymer over SPR and PL of Ag NPs, which showed that both act in opposite way from each other in each case. The Cu^{2+} cations were found to enhance SPR and suppress PL intensity, while PCz contributed to suppress SPR and enhance PL intensity, along with showing its own luminescence in violet region. In both cases PCz played a contributive role to counterbalance the effect of surface adsorbed cations, while in PL case, its role is particularly considerable to explore the possible electronic transitions within the surface atoms of Ag NPs and their interactions with surface adsorbed cations and surface coating polymer for future study.

Experimental

Chemicals

$AgNO_3$ (99.8%), ethylene glycol (96%), ethanol (99.8%), acetone (99.5%), acetonitrile (95%), were purchased from Beijing Shiji. PVP (K30) was bought from Fuchen Chemical Reagent Company, Tianjin. Carbazole monomer (95%) was bought from Shanghai Zhixin Chemical industry Co Ltd, and was recrystallized in 1:1 of n-hexane/isopropanol before use. Cupric acetate (98%) was bought from Beijing Yili Chemical Reagent Company.

Synthesis

Ag@PCz 3D nanocomposites were prepared chemically in two steps, first uniform Ag NPs were prepared using microwave energy and then carbazole was polymerized around the surface of as-prepared Ag NPs using Cu^{2+} cations as an oxidant. The whole process proved helpful to optimize the product in each step and also to study the optical behavior in systematic way. The process was briefly described as;

Synthesis of Ag nanoparticles

The Ag NPs were synthesized using microwave polyol method developed by Komarneni et al. [20]. The method was further optimized to get uniform Ag nanoparticles. Herein, 0.090 g $AgNO_3$ and 0.22 g PVP were dissolved in 20 mL ethylene glycol (EG), where EG served as solvent and reducing agent. The as-prepared solution was irradiated by 200 W microwaves, at 120 °C for 10 min on continuous stirring. The solution at advent turns into yellow color which changed to red, blue, green, and grey color, respectively, within 5 min. The time was further prolonged to 10 min for consistency. Later, product was washed using acetone and ethanol, and separated by centrifugation at 5000 rpm. In this way Ag NPs were successfully prepared, which were used for the next step as well as for morphological and optical characterization.

Synthesis of Ag@polycarbazole nanocomposites

The sufficiently washed Ag NPs were dispersed in $Cu(CH_3COO^-)_2$ solution in acetonitrile using ultrasonication for 10 min and then centrifuged again at the speed of 5000 rpm. In this way copper ions (Cu^{2+}) were adsorbed onto the surface of Ag NPs [21] and transformed into cations-loaded Ag nanoparticles, which became active for oxidative polymerization. These cations loaded NPs were used for SPR and PL analysis, and also mixed with 0.1 M, 20 mL carbazole solution, that was prepared in acetonitrile for further reaction. The mixture was heated at 50 °C for 3 days in closed box to avoid direct sun light as carbazole is a photosensitizer. The surface cations over Ag NPs polymerized carbazole in oxidative way, and the resultant PCz during growth process enclosed these NPs one by one and also interconnected them to some extent. Thus Ag@polycarbazole as a new nanocomposite material was obtained, which was washed by ethanol to remove monomer and remaining salt of copper, and then centrifuged to separate pure product.

Characterization

The shape and surface of Ag NPs and Ag@polycarbazole composite were characterized by using TEM (HITACHI-800 operated at 200 kV) and SEM (FEI XL-30ESEM-FEG) microscope. The PCz as a coating material was characterized by FT-IR (Bruker Tensor37) and Raman (Renishaw plc, UK equipped with a 25 mW (632.8 nm) He–Ne laser). The interfacial study was carried out by XPS (Thermo VG Escalab 250) and optical behavior of

Ag@polycarbazole nanocomposites was measured by UV–Vis (UV-3150 Shimadzu) and PL (Varian Cary Eclipse) spectrophotometer.

Results and discussion

The morphology and surface outlooks of Ag NPs and Ag@PCz nanocomposites were observed by TEM and SEM, respectively. The TEM picture displayed in Fig. 1a shows that Ag NPs are an exclusive product prepared in step one by using modified microwave polyol method. The inset in Fig. 1a shows magnified NPs from the same sample which duly represents the morphology, size, and surface outlook of these NPs. By the exquisite observation it is clear that the Ag NPs are pseudospherical in shape, 50–70 nm in diameter, and uncovered by surface. The Fig. 1b shows Ag@PCz nanocomposite that was obtained in second step where carbazole was polymerized around Ag NPs by using $Cu(CH_3COO^-)_2$ as an oxidizing agent. The sample was observed by TEM after complete washing by ethanol to remove monomer and other impurities, which demonstrates that core Ag NPs are completely covered by the light polymer material having 4–9 nm thickness which form a thin matrix around these Ag nanoparticles. From these observations it is also found that the polymer during growth process has enclosed Ag NPs one by one as shown in inset of Fig. 1b as well as interlinked them in enclosed form that developed polymer matrix around nanoparticles. Furthermore, surface of pristine Ag NPs and Ag@PCz nanocomposite was scanned by SEM to discover the effect of polymer encapsulation over the surface of uncovered (pure) nanoparticles. The SEM picture that was displayed in Fig. 2, illustrates that the surface outlook of pure Ag NPs is seemed to be relatively smooth (Fig. 2 inset) as compared to Ag@PCz nanocomposite. The surface outlook in composite form displayed distinct polymer outgrowths around particles, and particles are also seemed to be interconnected to some extent as already observed by TEM. Therefore, from these observations, it can be inferred that PCz is successfully grown around Ag NPs, which was desirable due to its high thermal stability, broad range of optical properties, and coherent film making ability. Furthermore, its one by one growing tendency around each Ag NPs is beneficial to reduce the possibility of bare surface touch within Ag NPs that is a major cause of coalescence.

The PCz as a coating material over Ag NPs was further characterized by FT-IR and Raman measurements. The FT-IR characterization, which is shown in Fig. 3a, relates the bands present at 3434, 1629, and 1414 cm^{-1} for N–H stretching, aromatic ring stretching, and C–N stretching vibrations, respectively. The band that appears at 1557 cm^{-1} stands for doped polycarbazole. The weak bands

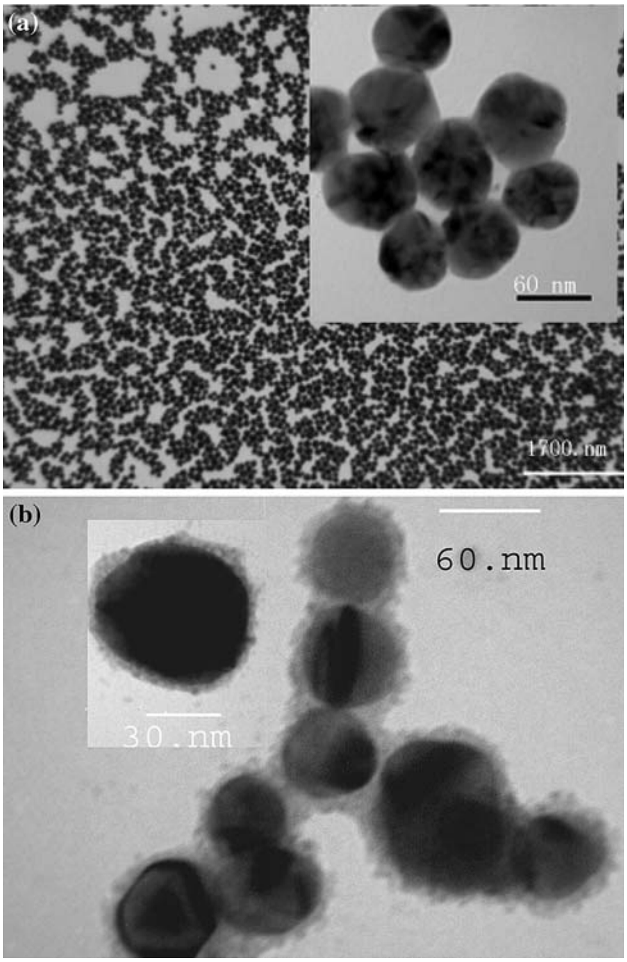

Fig. 1 TEM pictures of Ag NPs (**a**), and Ag@PCz nanocomposite (**b**)

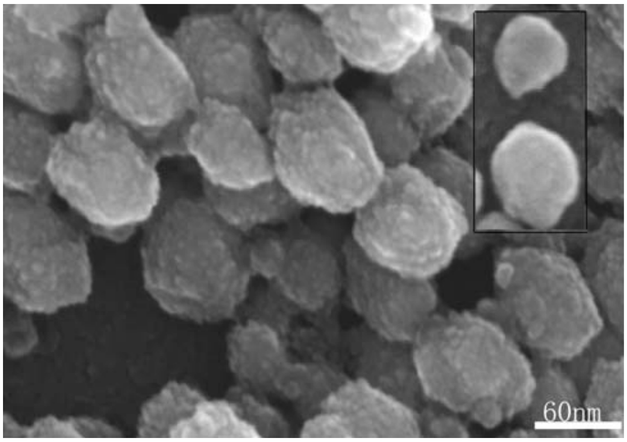

Fig. 2 SEM picture showing surface appearance of Ag@PCz nanocomposite while the inset is displaying surface appearance of pure Ag NPs

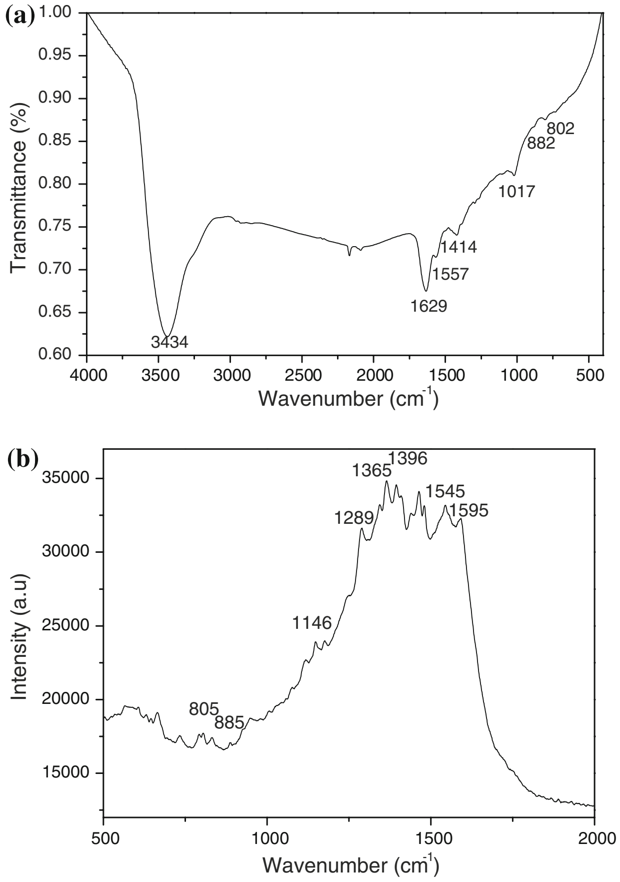

Fig. 3 FT-IR and Raman bands of Ag@polycarbazole nanocomposite are shown in (**a**) and (**b**), respectively

appear at 802 and 882 cm^{-1} are characteristics bands for 3,6 polycarbazole [22]. The peak's morphology displayed in FT-IR measurement are seemed to be greatly influenced by core Ag NPs; therefore, Raman measurement was used as a supporting tool due to its surface enhanced resonance (SER) effect in such systems. The Raman observations which are shown in Fig. 3b, relate 1595 to 1545 cm^{-1} as C=C stretching vibrations and 1396 to 1345 cm^{-1} as C–C stretching vibration [23, 24]. The splitting of peaks may be due to oxidized and neutral state of polymer around the Ag particles. The band that appears at 1461 cm^{-1} stands for C–N stretching vibration and the vibrations from 1100 to 1290 cm^{-1} stand for C–N stretching along with C–H bending modes. The peaks from 800 to 950 cm^{-1} region illustrate the substituted aromatic ring of carbazole and in-plane C–H deformation [25]. In this region, the existence of peaks at 805 and 885 cm^{-1} is corresponding to para-substitution that stands for 3,6 polycarbazole [22]. On the basis of these characterizations, it can be inferred that Ag@polycarbazole nanoparticles were successfully fabricated as a new nanocomposite material, where Ag NPs are present as a core material and PCz wrap them. The FT-IR and Raman measurements further elucidated that polymer exist in form of 3,6 polycarbazole as a coating material.

Moreover, XPS was used to study the interface between Ag surface atoms and PCz by measuring the binding energy of silver and carbon, and also by comparing peak's morphology and intensity. The binding energy of silver was measured for pristine Ag NPs and Ag@polycarbazole nanocomposite, which is displayed in Fig. 4a, b, respectively, while the binding energy of carbon is shown in Fig. 4c. According to Fig. 4a, b, the binding energies of silver for pure Ag NPs corresponding to $3d_{5/2}$ and $3d_{3/2}$ are located at 367.3 and 373.3 eV having peak intensity ratio ($3d_{5/2}/3d_{3/2}$) 1.3, while for Ag@polycarbazole nanocomposite, this binding energy having same peaks intensity ratio, is located at 368.5 and 374.5 eV. On comparing Fig. 4a, b, it was found that peaks morphology and peaks intensity ratio in both cases are identical; the binding energy of Ag in nanocomposite form is 1.2 eV blue shifted, and the intensity of peaks in nanocomposite form is greatly decreased. The identical peaks morphology and peaks

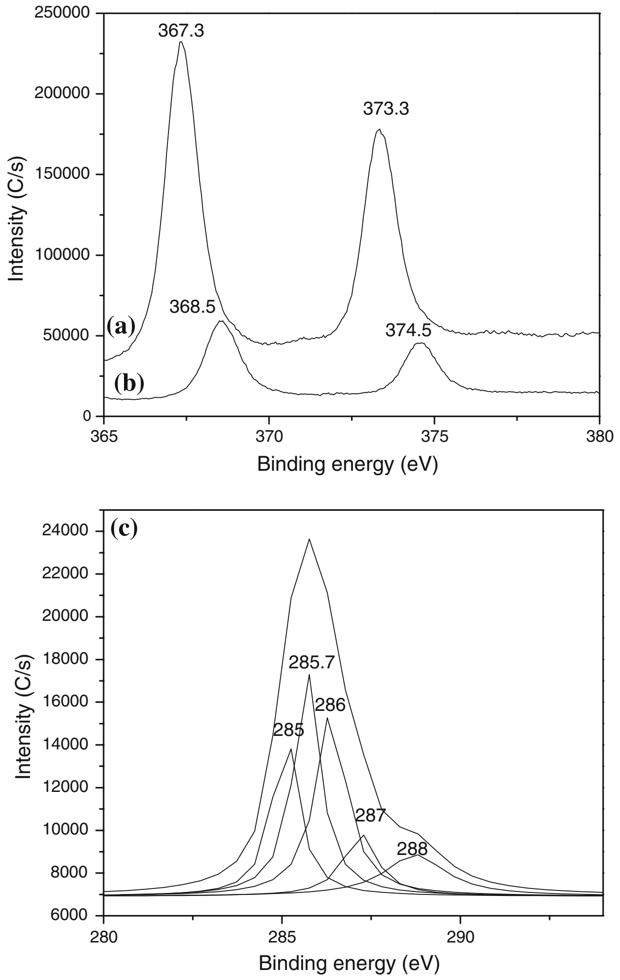

Fig. 4 XPS measurement of binding energy for pristine Ag NPs (**a**), Ag@polycarbazole NPs (**b**), and carbon (**c**)

intensity ratio of nanocomposite to pure Ag NPs relates that at interface, nano-Ag surface atoms have not undergone to any chemical change and they exist in the form of pure Ag atoms. The blue shift of binding energy in Ag@PCz nanocomposite was found very close to the standard binding energy of Ag, which is reported as 368.3 and 374.3 eV for the same core orbitals [1, 24]. Therefore, the blue shift demonstrates the gain in stability of nano-Ag surface atoms due to surface polymer which brought these atoms to possible equilibrium position that was lost in pure form due to band narrowing effect, in which these surface atoms experience net inward attraction as compared to the bulk form [26]. Moreover, decrease in intensity in composite form is referred to surface covering of Ag NPs, which in turn reduced the number of Ag atoms underlying the X-ray scan of XPS measurement. As the C is main element in PCz so XPS was also used to measure the binding energy of C that is displayed in Fig. 4c. The C signal was deconvoluted into five peaks, where the binding energies located at 285, 285.7, and 286 eV are assigned to C–C, C=C, and C–N, while the peaks found at 287 and 288 eV are corresponding to carbonyl and carboxylate carbon, which are present as dopant from oxidizing agent [25, 27].

At the end, the novel optical phenomenon of Ag NPs and Ag@PCz nanocomposite was explored by systematic UV–Vis and PL analysis. Herein, the effect of Cu^{2+} adsorption and polymer encapsulation over SPR and photoluminescence of Ag NPs was examined. The UV–Vis measurement displayed in Fig. 5a, b, and c relates to SPR absorption of pure Ag NPs, Cu^{2+}-loaded Ag NPs, and PCz encapsulated Ag NPs, respectively. The SPR maxima of pristine Ag NPs is located at 446 nm, which is due to out-of-plane dipole resonance band [28], and on doping with Cu^{2+} the intensity increased from 1.2 (a.u) to 2.8 (a.u) with slight red shift. However, after PCz encapsulation, it decreased up to 0.2(a.u), that is less as compared to both, pure Ag NPs and Cu^{2+}-loaded Ag NPs. Herein, SPR is found quite sensitive to the surface composition of Ag NPs, where its intensity increased on doping with Cu^{2+} and decreased due to polymer growth. The SPR arise due to collective oscillation of conduction band electrons with electromagnetic radiation [29], which demonstrated reverse effect on its intensity on doping with Cu^{2+} and polymer growth. These observations support that Ag NPs possess potential application to detect copper cations (Cu^{2+}) and organic moieties around its surface due to its sensitive SPR behavior. Similarly the photoluminescence of Ag NPs, Cu^{2+}-loaded Ag NPs, and PCz-sheathed Ag NPs was compared which are displayed in Fig. 6a, b, and c. respectively. These samples having same concentration were irradiated by 255 nm UV light. According to the results, Ag NPs produced emissions at 426, 485, and 512 nm, and the luminescence of Cu^{2+}-loaded Ag NPs was found on same positions, but having considerably lower intensity. However, after forming a composite with PCz, the PL intensity increased well up to blue region (485 nm) along with additional emission at 400 nm as shown in Fig. 6c. In this case, the PL intensity at 512 nm is higher than Cu^{2+}-loaded Ag NPs, but less than pure Ag nanoparticles, which maybe a concentration difference, i.e., the concentration of Ag NPs in nanocomposite is expected to be less as compared to pure Ag NPs in the same volume. As PCz gives luminescence only in violet and blue region [18], so it does not affect the PL intensity of Ag NPs at 512 nm position, which fall in green region. From these observations it is found that PCz is useful to counterbalance the effect of surface cations over PL intensity of Ag

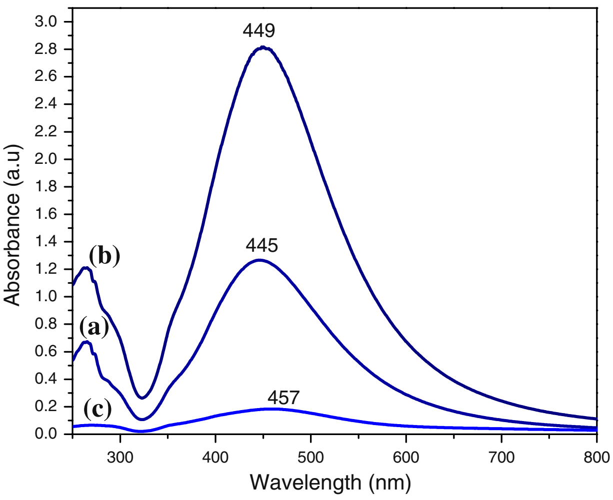

Fig. 5 UV–Vis absorbance of Ag NPs (*a*), cation-loaded Ag Nps (*b*), and Ag@PCz nanocomposite (*c*)

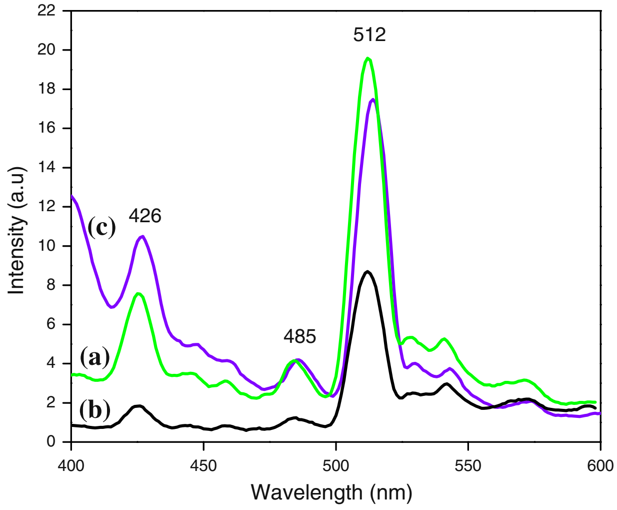

Fig. 6 PL behavior of Ag NPs (*a*), Cu^{2+}-loaded Ag NPs (*b*), and Ag@PCz nanocomposite (*c*)

nanoparticles. Furthermore, it is also useful to produce and enhance luminescence from violet to blue region. As the PL arise due to electronic transition between upper d-band and conduction sp-band in noble metals [30], therefore, the effect caused by surface cations and polymer to the electronic transitions is helpful to explore the detailed PL mechanism in Ag NPs as well as in Ag@PCz nanocomposite. It is further helpful to study state density and quantum confinement of electrons in nanomaterials.

Moreover, the SPR and PL behavior of Ag NPs does not act in similar trend, in first case SPR intensity increased on Cu^{2+} adsorption and decreased after polymer coating, while in second case PL intensity decreased due to Cu^{2+} adsorption and increased due to polymer coating. In both cases the conduction sp-band is influenced by Cu^{2+} adsorption and polymer encapsulation; therefore, this study would be helpful to discover the role of conduction band electrons to get further insight in nano-optics [31], which is a promising research area of nanooptical phenomenon.

Conclusion

Ag@PCz nanocomposite having novel optical properties was prepared as a new material. The as-prepared product is pseudospherical in shape, 50–70 nm in diameter, and entirely encapsulated by 3,6 polycarbazole. In Ag@PCz nanocomposite, PCz was found contributive to bring the nano-Ag surface atoms toward their most stable position as demonstrated by XPS measurement. Moreover, the SPR and PL behavior of Ag NPs were found to be affected by Cu^{2+} adsorption and polymer encapsulation in opposite way, i.e., Cu^{2+} adsorption significantly increased SPR intensity and polymer coating suppressed it, while PL intensity decreased due to Cu^{2+} adsorption and increased due to polymer encapsulation. This behavior would be helpful to explore the optical mechanism in more sophisticated way. Furthermore, the composite synthesis proved advantageous to combine the luminescence behavior of Ag NPs and PCz moieties, which produced emissions at 400, 426, 485, and 512 nm wavelengths on single excitation energy.

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