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Influence of Different Preparation Methods of Silver-Modified Carbon Nitride on the Photocatalytic Activity towards Indigo Carmine Dye

Ladislav Svoboda^{1,2, a*}, Richard Dvorsky^{1,2, b}, Jiri Bednar^{1,2, c}, Dalibor Matysek^{3, d}, Marketa Pomiklova^{4, e}

¹IT4Innovations National Supercomputing Center, VSB – Technical University of Ostrava, Ostrava, 17. listopadu 15/2172, Ostrava 708 33, Czech Republic

²Nanotechnology Centre, VSB – University of Ostrava, 17. listopadu 15/2172, Ostrava 708 33, Czech Republic

³Institute of Geological Engineering, VSB – Technical University of Ostrava, 17. listopadu 15/2172, Ostrava 708 33, Czech Republic

⁴TEM laboratory, Public Health Institute of Ostrava, Partyzanske namesti 2633/7, Czech Republic

^aladislav.svoboda@vsb.cz; ^brichard.dvorsky@vsb.cz; ^cjiri.bednar@vsb.cz;

^ddalibor.matysek@vsb.cz; ^emarketa.pomiklova@zuova.cz

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Abstract. Silver nanoparticles (Ag NPs) may increase photocatalytic activity of widely used photocatalysts under visible light irradiation and decrease recombination probability of photogenerated electrons and holes. In this paper, we report three different preparation methods to obtain Ag/C₃N₄ nanocomposites. We used Ag nanoparticles a) synthesized by using sodium borohydride, b) synthesized by using UV 365 nm LED and c) already prepared and purchased from company Nano Iron. The Ag NPs have been loaded on thermally exfoliated carbon nitride with the aim to form 5 wt.% Ag/C₃N₄ nanocomposites. Further their photocatalytic activity was tested towards Indigo carmine dye (IC) under 416 nm LED. The results show that method a) loaded different amount and size of Ag NPs on the surface of C₃N₄, b) changed optoelectronic behaviors of nanocomposites and c) significantly influenced their photocatalytic activity.

Introduction

Carbon nitride belongs to group of organic semiconductors with indirect band gap (2.7 eV). This material seems to be promising candidate for photocatalytic reactions due to its outstanding thermal and chemical stability, low-cost method of preparation and its good response to visible-light radiation due to narrow band gap. Nevertheless, because of the fast recombination of photogenerated electrons and holes, the photocatalytic activity is still low [1]. In the past, several research groups modified C₃N₄ with CdCO₃ [2], ZnFe₂O₄ [3] or Fe(II) [4] and tested photocatalytic activity towards indigo carmine dye.

At the presence, Ag NPs are widely used in different industries and applications such as antimicrobial coatings [5]. The interesting properties of Ag NPs combined with semiconductor relies on silver's ability in acting as a sink for electrons. When semiconductor such as C₃N₄ is in contact with metal NPs, there is creation of a Schottky barrier that facilitates movement of electrons from C₃N₄ to metal due to different positions of Fermi level in both materials. This enhances separation of photogenerated electrons and holes and suppresses their recombination rates. The movement of electrons leaves additional positive holes on semiconductor, which are capable of oxidizing organic contaminants [6]. Such metal/semiconductor system is often influenced by the amount and size of metal NPs on the surface of semiconductor.

The aim of this work was to evaluate the effect of three different preparation methods and their influence on the properties of Ag NPs in the Ag/C₃N₄ nanocomposite and their photocatalytic activity towards aqueous solution of indigo carmine dye.

Experimental Section

Chemicals and Reagents. Silver nitrate (99.8%) was purchased from Penta, Melamine ($\geq 99\%$) and sodium borohydride (NaBH_4 , 96%) were purchased from Sigma-Aldrich and Ag nanoparticles with median particle size 20 nm was purchased from Nano Iron, s.r.o. All chemicals used in this study were analytical grade and were used as received without further purification. For all the preparation of solutions, deionized water was used.

Material Synthesis

Synthesis of C_3N_4 . Exfoliated C_3N_4 was prepared by thermal treatment of bulk C_3N_4 . Both materials were prepared according to our previous work [1].

Synthesis of 5 wt. % Ag/ C_3N_4 . *1. method:* Ag NPs were synthesized by adding 186 μL of 0.5 M silver nitrate into the vigorously stirred deionized water (100 mL) containing 190 mg of C_3N_4 . After 30 minutes, solution was vigorously stirred and irradiated with UV LED with maximum emission at 365 nm for 1 hour. *2. method:* Ag NPs were synthesized by adding 186 μL of 0.5 M silver nitrate into the vigorously stirred deionized water (100 mL) containing 190 mg of C_3N_4 . After 30 minutes 0.2 mL of 1.5 M sodium borohydride was added and the solution was stirred for next 1 hour. *3. method:* 100 mL of purchased solution with average 20 nm Ag NPs ($c = 100$ ppm) was added into the vigorously stirred deionized water (100 mL) containing 190 mg of E- C_3N_4 for 1 hour. After 1 hour, each solution was three times centrifuged and washed by deionized water. Finally, all solutions were rapidly frozen and freeze-dried. Final samples were denoted as S1 prepared by 1. method, S2 prepared by 2. method and S3 prepared by 3. method. For comparison, C_3N_4 material was treated as sample S1 without the presence of silver nitrate and irradiation. Final sample was denoted as E- C_3N_4 .

Evaluation of Photocatalytic Activity

The photocatalytic activity of prepared photocatalysts were performed using aqueous solution of IC under 416 nm visible light irradiation. All photodegradation experiments were performed at a temperature of 25 °C and at pH 7. The amount of used photocatalyst was 30 mg, which was dispersed in 30 mL of aqueous solution of IC ($c = 5$ mg L^{-1}). Residual concentration of IC was determined from absorbance obtained by using UV-Vis spectrometer OCEAN OPTICS USB4000.

Material Characterization

X-ray powder diffraction patterns were measured using a Bruker D8 Advance diffractometer (Bruker AXS). Phase composition of the samples was evaluated using PDF 2 (Release 2011) database (International Centre for Diffraction Data). The final nanostructures were studied by scanning electron microscopy SEM FEI Quanta 650 FEG and transmission electron microscopy Jeol JEM 1230, operating at 80 kV. The optical absorption of the powder solids was obtained by measuring respective UV-Vis DRS spectra with a Shimadzu UV-2600 (IRS-2600Plus) spectrophotometer. Spectrometer FLS920 (Edinburgh Instrument Ltd, UK) was used for registration of photoluminescence spectra.

Results and Discussion

XRD Analysis. The XRD analysis of E- C_3N_4 , S1, S2 and S3 nanocomposites are shown on Fig. 1. The diffraction peak at 2θ of 11.5° and 28° are the characteristic peaks of C_3N_4 with diffraction planes (100), (002) respectively. Four silver peaks observed at 38.1° (111), 44.3° (200), 64.5° (220) and 77.4° (311) assigned to face centered cubic (FCC) structure (PDF 03-065-2871) were observed in patterns of samples S2 and S3. Due to very small size of Ag NPs and their small amount in sample S1 all four peaks typical for Ag could not be detected. According to EDX analysis sample S1 contained 0.54-0.78 wt. % of Ag NPs, S2 contained 0.77-1.3 wt. % and S3 contained the highest amount of Ag NPs 3.84 – 4.98 wt. %.

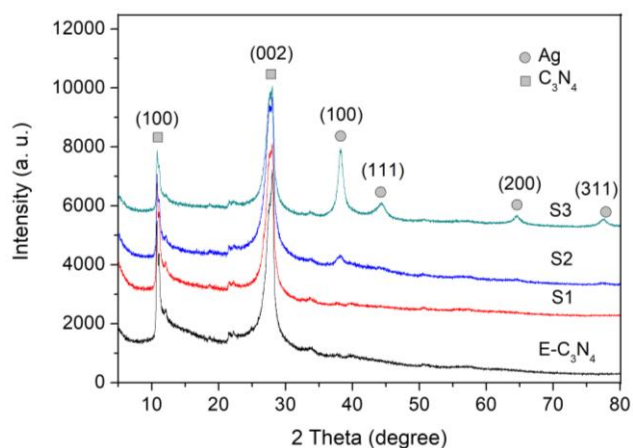


Figure 1. XRD patterns of E-C₃N₄, S1, S2 and S3 composites

Transmission and Scanning Electron Microscopy (TEM/SEM) Analysis. Fig. 2 shows typical TEM image of nanocomposite S1. In this composite Ag NPs are small dark dots distributed on the surface of well exfoliated thin layers of C₃N₄. The estimated particle size was estimated around 2-3 nm. Small amount of observed particles indicating that the content of deposited Ag NPs is less than aimed 5 wt. % of Ag. However, particle size about 2-3 nm was above our expectation. TEM images confirmed that most of the particles did not aggregate together during preparation of nanocomposite S1. Small particle size was caused by using less effective reduction pathway.

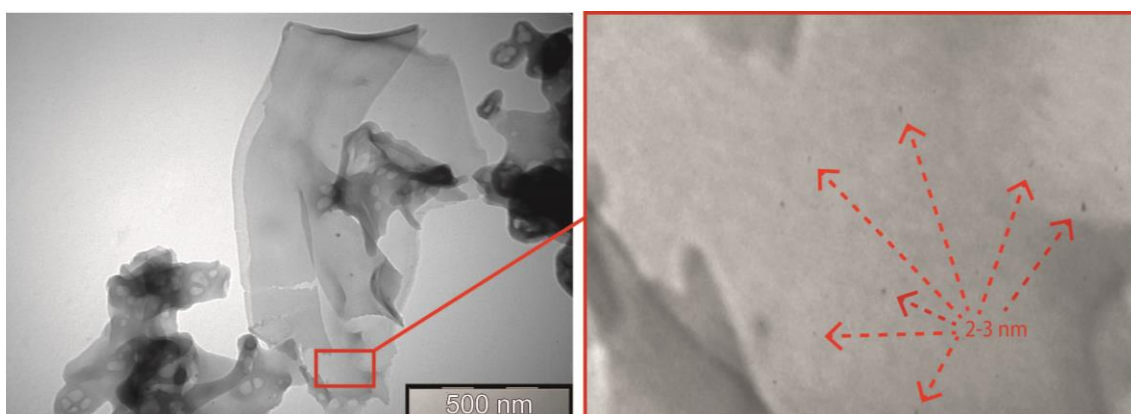


Figure 2. TEM images of nanocomposite S1 (left) with zoomed area on its layer (right)

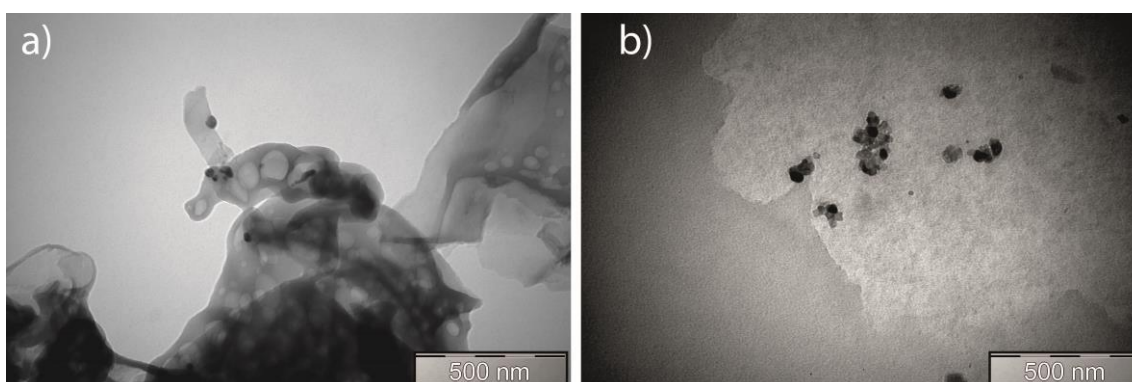


Figure 3. TEM images of nanocomposites a) S2 and b) S3

The reduction took a place only for Ag cations adsorbed on the surface of C₃N₄. For enhancing photo-induced synthesis, a secondary source of electrons and longer time of irradiation is required [7]. TEM images of other nanocomposites (S2 and S3) are shown in Fig. 3. As we can see 2nd and 3rd method created bigger Ag NPs. Samples S2 contained also small amount of Ag NPs but with bigger particle size ranging from 20 nm to 40 nm. Rapidly added NaBH₄ created high chemical potential, this

caused nucleation and further immediately agglomeration of Ag NPs. Sample S3 contained Ag NPs (20-50 nm) as we used already prepared commercial Ag NPs with such particle size distribution.

UV-Vis Analysis. The UV-Vis absorption spectra of all samples are depicted on Fig. 4a). All Ag-modified C_3N_4 samples showed LSPR band located around 475 nm and sample S3 also a band located at 550 nm indicating that the amount and size of Ag NPs in the final nanocomposite is completely different. The Tauc plots are shown in Fig. 4b). The band gap energy values follow order $E-C_3N_4 = S1 > S2 > S3$ ($2.95 \text{ eV} = 2.95 \text{ eV} > 2.88 \text{ eV} > 2.57 \text{ eV}$). It was found that the band gap decreases as the Ag NPs concentration is increased. This is due to the interaction between the Ag and C_3N_4 , where Ag NPs caused the creation of trap levels between the conduction bands and valence bands of C_3N_4 .

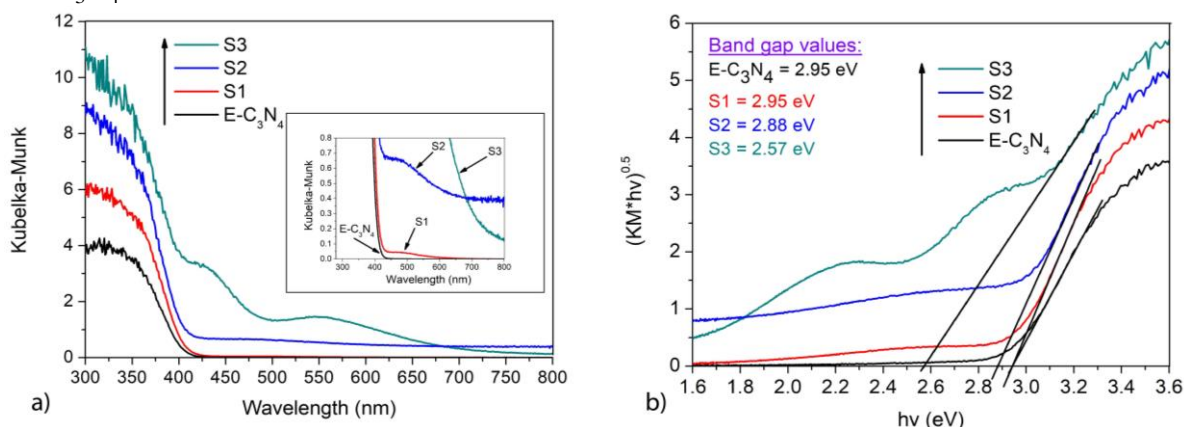


Figure 4. a) UV-Vis absorption spectra and b) Tauc plots with estimated band gap values of E- C_3N_4 , S1, S2 and S3 composites

Photoluminescence Analysis. Fig. 5 shows the PL spectra of the E- C_3N_4 and the Ag/ C_3N_4 nanocomposites excited at 325 nm. The emission peak of samples at around 430 nm was quenched in intensity as Ag content and particle size increased. This emission is caused by recombination of electrons and holes in C_3N_4 . By adding acceptor of electrons such as Ag NPs, the recombination probability is lower. Although the amount of Ag NPs in nanocomposite S1 was only around 0.5 wt. %, the emission intensity was quenched almost by a half. This indicating very high efficiency of deposited Ag NPs to act as electron acceptors. Higher amount of Ag in other samples caused even higher decrease of photogenerated emission in C_3N_4 .

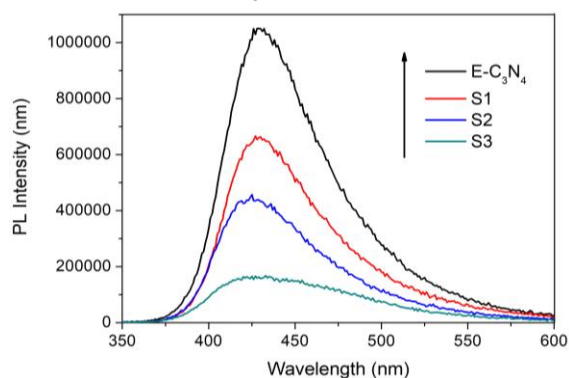


Figure 5. Photoluminescence spectra of E- C_3N_4 , S1, S2 and S3 composites

Photocatalytic Activity Evaluation. The photocatalytic activity was increasing in order S3, S2, E- C_3N_4 and S1 with observed kinetic rate values $k_{S3} = 0.0077 \text{ s}^{-1}$, $k_{S2} = 0.0167 \text{ s}^{-1}$, $k_{E-C_3N_4} = 0.0333 \text{ s}^{-1}$ and $k_{S1} = 0.0549 \text{ s}^{-1}$. This clearly indicates that the introduction of Ag NPs on the surface of C_3N_4 can positively influence its photocatalytic activity if the amount of silver is a) not too high (0.5 wt. %) and b) in small sizes distributed over whole surface of C_3N_4 . Photocatalytic activity of pure C_3N_4 is mostly attributed through reduction of adsorbed oxygen on the surface of C_3N_4 due to insufficient oxidation potential of the holes to generate hydroxyl radicals [8]. However, photogenerated holes can decompose IC directly. Decreasing recombination probability of electron-holes by introducing Ag

can increase amount of active holes on the surface of nanocomposite and thus enhance photocatalytic activity (sample S1). If the amount of silver is too high, the amount of free electrons for oxygen reduction to superoxygen radicals is less and the photocatalytic activity is lowered.

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Summary

In this work, we successfully synthesized and characterized three different Ag/C₃N₄ nanocomposites. Even that the amount of silver precursor was similar, the wt. % of Ag on the surface of C₃N₄ was different. By mixing Ag NPs, the photocatalytic activity was the worst due to their agglomeration and due to trapping photogenerated electrons, which cannot be further used for photocatalysis. Similar trend was observed for Ag NPs prepared by reduction reagent NaBH₄. By using UV irradiation, the final amount of Ag NPs in final nanocomposite was lower than was intended (only 0.54 - 0.78 wt. %), but such prepared Ag NPs were very small (2-3 nm) and modified C₃N₄ showed the best photocatalytic activity, which was two-times higher than pure E-C₃N₄. The highest photocatalytic activity was observed for sample S1 reaching observed kinetic rate $k = 0.0549 \text{ s}^{-1}$.

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