



Fig. 4. (A) TEM image of silver/polyelectrolyte soaked in PIC for 24 hours. (B) Experimental absorbance spectra of PIC coated Ag core-polyelectrolyte shell nanoparticles, with varying polyelectrolyte layer thickness. 1 (PDADMAC/PSS) (blue curve), 2 (PDADMAC/PSS) (red curve), and 3 (PDADMAC/PSS) (green curve) correspond to 2, 4, and 6 alternating layers of PDADMAC and PSS, respectively. Formation of the red-shifted J-aggregate peak was observed at 581 nm, 581 nm, and 579 nm for the Ag/1(PDADMAC/PSS)/PIC, Ag/2(PDADMAC/PSS)/PIC, and Ag/3(PDADMAC/PSS)/PIC nanoparticles, respectively. (C) Simulated absorbance spectra for the impact of spacer layer thickness on the absorption wavelength of the J-aggregate peak. An oscillator strength (f) of 0.35 and a relaxation rate (γ) of 0.015 were assumed in the calculations.

The J-aggregate peaks were observed at wavelengths that were comparatively longer than what is commonly reported in the literature for PIC, i.e. 575 nm. Additionally, the J-aggregate peak wavelength was found to increase with decreasing spacer thickness. These results suggest that the PIC was fully, or close to fully aggregated, and that the plasmon-exciton interaction further red shifted the J-aggregate peak. This observation is consistent with the fact that plasmon-exciton interactions are enhanced as the distance between the J-aggregate shell and the Ag core particles is diminished.

Simulated absorbance spectra of Ag/(PDADMAC/PSS)/PIC nanoparticle composites were calculated in Fig. 4(c) in order to explain the main absorption features of the experimental data. For the dielectric constants, we used experimental frequency-dependent complex dielectric constant for the silver [33], literature values of 2.25 for PDADMAC and 2.56 for PSS [34], and Eq. (8) (with $f = 0.35$ and $\gamma = 0.015$) for the PIC J-aggregate. We assume a silver core of 54.5 nm (with SD = 9.8 nm), a J-aggregate dye outer shell of 5 nm, and a polyelectrolyte spacer of thickness 1 nm per bi-layer. This calculation is consistent for similar structures, in which the thickness of the polyelectrolyte bi-layers was determined to be 1.7 to 3.0 nm [21,34]. The simulation result in Fig. 4(c) was in qualitative agreement with the experimental absorbance spectra in Fig. 4 (b). Namely, the experimental and simulation results demonstrate the dependence of coupling strength and shift of the exciton frequency on spacer layer thickness. The red-shifted energy of the J-aggregate peak increases as the spacer layer thickness is minimized, i.e. the plasmon-exciton interaction is maximized. Discrepancies between the experimental and simulated results, in terms of J-aggregate peak shape, may be attributed to the fact that non-spherical and/or aggregated particles were not included in the simulated results.

5. Conclusion

Multilayered plexcitonic nanoparticles composed of an Ag core, polyelectrolyte spacer layer, and a PIC outer shell have been synthesized. The optical properties of the composite nanoparticles in aqueous solution were measured in the UV/Visible regions. Absorbance spectra of the colloidal nanoparticles indicate that PDADMAC/PSS spacer layers successfully promoted the J-aggregation of PIC. The in situ generation of the J-aggregate was observed when PIC standard was added directly to a colloidal suspension containing silver core – polyelectrolyte shell composite nanoparticles. The formation of the fully J-aggregated form was observed when PIC was exposed to a colloidal suspension of silver core – polyelectrolyte shell nanoparticles for 24 hours. The 24 hour study yielded a J-aggregate absorbance at 579-

581 nm, indicating the formation of a fully aggregated dye on the surface of the composites. The fully aggregated form of PIC is typically observed at 575nm. The additional red-shift in energy that was experimentally observed may be explained by the plasmon-exciton interaction between the silver core and the J-aggregate exterior. It is concluded that the use of oppositely charged polyelectrolytes is a valid approach for inducing the formation of J-aggregates on silver core-polyelectrolyte shell particles. Furthermore, polyelectrolyte spacer layers are a means of controlling the plasmon-exciton distance, which can ultimately be used to control the shift in exciton frequency. Finally, the ease with which polyelectrolyte layers are assembled onto colloidal nanoparticles of varying shape and composition, makes this technique suitable for building a wide range of plexcitonic particles.

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