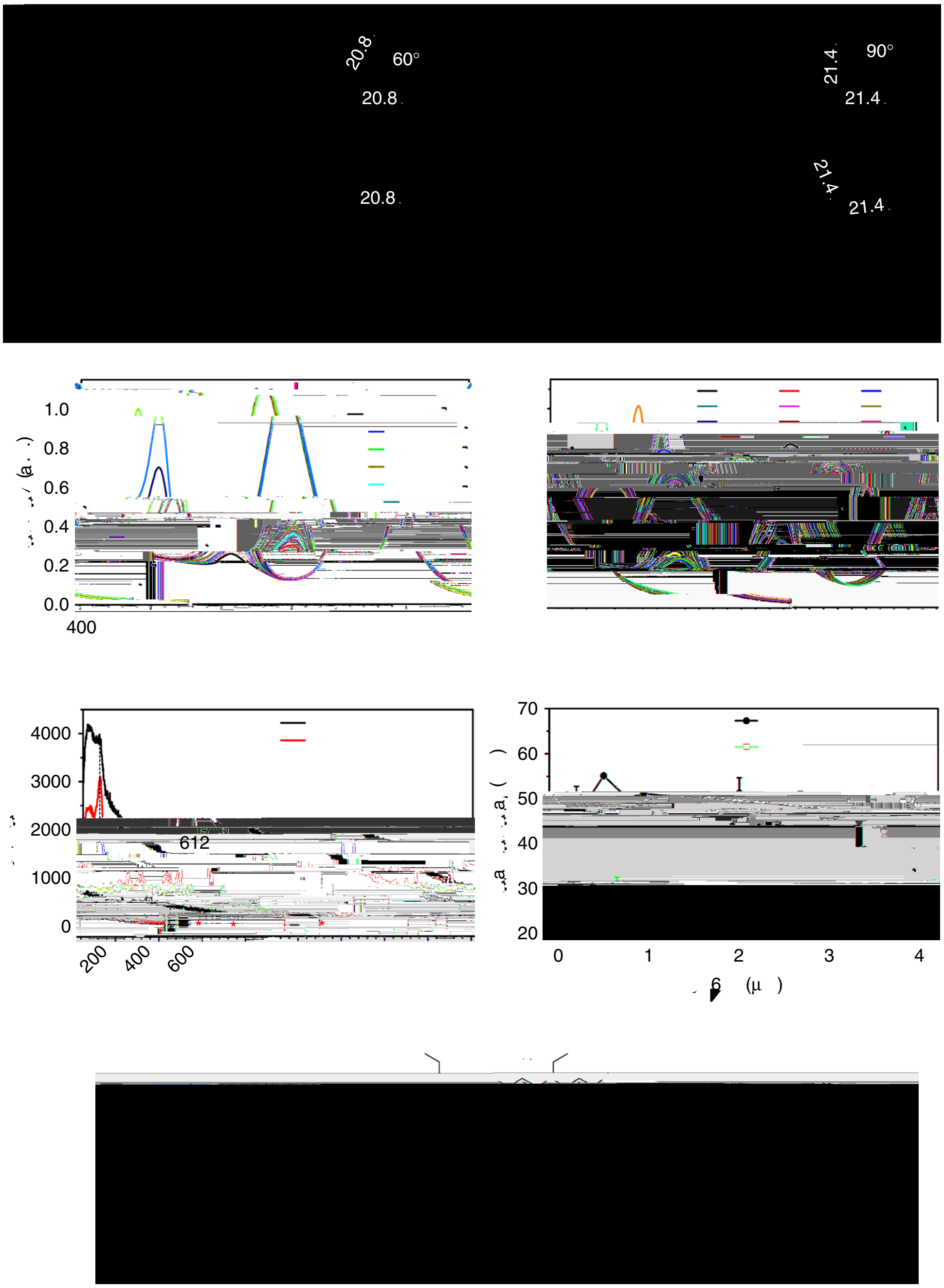
Self-assembly is a ubiquitous phenomenon in nature, creating the diversity of materials and organisms. However, the functionalities and structural complexity of artificial self-assembly are dwarfed by the counterparts in nature, especially in the nanoscale. With rapid development of nanotechnologies, nanoparticle self-assembly exhibits great potentials in bio-assays, optoelectronic devices, sensors, solar cells and so forth[1–7] insights into the thermostability of the tetragonal superlattice, we have performed in situ observations with annealing temperature from 260–310 °C (Fig. 2g). In this temperature range, the tetragonal symmetry remains. However, with increasing temperature, the structural integrity of tetragonal superlattices is gradually destroyed. To confirm that the adsorbed R6G is responsible for the enhancement of thermostability of tetragonal superlattice, we have performed its Raman spectra. Owing to the plasmonic



hotspots in the tetragonal superlattice, much stronger R6G Raman signals in tetragonal superlattice are detected (Supplementary Fig. 4) than those of the discrete GNRs dispersed in the aqueous solution (Fig. 1e), suggesting the confinement of R6G between the adjacent nanorods. Furthermore, such Raman signals even can be observed after 250 °C thermal annealing, indicating the critical role of R6G in maintaining tetragonal superlattice.

superlattice, four nanorods are linked face-to-face and the cross-section of nanorod can be described as an octagon. Further, HRTEM images show the side facets are linked by {100} or {110} ones. Based above TEM observations, we consider nanorod is surrounded by four {100} and four {110} side facets. Adsorption energies for R6G on Au{110} and Au{100} facets are similar (Supplementary Table 1), suggesting that adsorption of R6G on these two facets is equivalent. Obviously, the alignment of two nanorods with larger facets face-to-face can guarantee more R6G chains formed between two nanorods no matter the larger facet is {110} or {100} facet. If {110} facet is larger, two nanorods with o528.63osit54.6019878({110})-392.01702441(are)ts abovcrinot524.799-528.79

dimer. The probability of forming different superlattices can be correlated to the overlap area between two neighboring facets in tetragonal and hexagonal superlattices with two {110}–{110} dimers (Tetra-1 and Hexa-1, Fig. 3f). The overlap area (red shadow, Fig. 3f) between two {110}–

plasmon modes will occur in the multilayer of the tetragonal superlattice. Experimentally, by tuning assembly conditions, we also obtain the multilayer of GNR tetragonal superlattice (Fig. 4h, i), in which the GNRs between the neighboring layers align head-to-head (Fig. 4j). The unique head-to-head alignment between neighboring layers affords an experimental solution for a simulated novel nanolens, which is made of stacked silver nanorods (50 nm-long nanorods head-to-head alignment with a

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