Chapter 5
Interactions of Nanomaterials with Plant Pigments

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Abstract The applications of engineered nanomaterials continue to expand into agri-food production, particularly in relation to nano-enabled agriculture formulations and/or colloidal particles. The widespread use of nanomaterials has generated concerns given the impact these nanostructures could be having on biomolecules,

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cellular homeostasis, and internal compounds. Understanding the interaction mechanisms between engineered nanomaterials and plant pigments is essential for unbiased assessments of their internalization, trafficking, behavior, and fate into cellular structures through a molecular lens. This chapter describes the mechanisms that drive these interactions on the cellular uptake and trafficking of nanomaterials. Furthermore, we discuss different examples of how plant photosynthetic and non-photosynthetic pigments can helpful to understand the behavior of nanomaterials in distinct plant tissues. Finally, we demonstrate some experimental (in vitro) and theoretical (in silico) methods aimed at monitoring and understanding existing molecular interactions of nanomaterials with plant pigments.

Keywords Engineered nanomaterials · Molecular interaction · Pigments · Plant systems · Homeostasis · Nanotoxicity · Environmental chemistry

5.1 Introduction

The growth of the nanotechnology sector has raised concerns about its environmental impacts. The release of nanomaterials (NMs) into the environment may induce potential adverse effects on natural ecosystems. In particular, terrestrial plants, which are the primary producers of the global food chain, are severely affected by NMs, raising concerns about this theme. Nanotechnology has shown great potential for addressing productivity problems in the agri-food sector (White and Gardea-Torresdey 2018; Bartolucci et al. 2022; Kandhol et al. 2022). Consequently, nano-enabled plant protection products can play an important role in the future of agriculture (Grillo et al. 2021; Pontes et al. 2021). Understanding the interaction mechanisms of NMs with plant pigments is crucial for unraveling their potential side effects on the metabolism, biochemistry, and physiology of these organisms when NMs are internalized. Negative cellular feedback related to nanostructured materials interactions with pigments can trigger complex allosteric adjustment responses or impair their metabolic pathway when extrapolating the homeostatic normal range (Santiago et al. 2020). The adjustment of cellular responses is related to their homeostatic ability. Thus, any structural or functional changes in plant pigments, particularly photosynthetic ones, impact the photosynthetic performance and biomass productivity (Tighe-Niera et al. 2018). Such nanomaterial–pigment interactions may represent a novel opportunity to increase crop production.

Plant organisms can produce more than 200,000 different types of chemical compounds (Fiehn 2002; Čepulytė and Būda 2022). Colored compounds are a special class, called "pigments," and include flavonoids/anthocyanins, betalains, carotenoids,

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and chlorophylls (Mulder-Krieger and Verpoorte 1994). The interaction of nanoarchitectured materials with plant pigments has been studied in the last decades, with important advances in several areas such as industry, fiber dying, medicine, pharmacology, food, and others (Shaid-ul-Islam and Mohamad 2013; Venil et al. 2020; Yu et al. 2021). Although, nanoparticle–pigment interaction has been explored and exploited extensively, few reports have systematically presented the mechanisms involved such as the factors affecting this interaction and their effects on plant fitness. Nanoparticles (NPs) have been implemented in agricultural systems as nanofertilizers and nanopesticides for crop growth regulation and disease control, respectively (White and Gardea-Torresdey 2018; Grillo et al. 2021; Lima et al. 2022). Consequently, due to their uptake and internalization, their interaction with biological molecules onto cellular media is expected.

Natural organic pigments are colored compounds produced by some organisms with a wide range of biological finality, i.e., communication, protection, reproduction, and others. In plants, pigments play a key role in light absorption for chemical energy production due to their physical properties of light absorption, trapping, and transport in the visible region of the electromagnetic spectrum. Depending on their chemical structure, pigments are responsible for a great variety of colors and fragrances of flowers, fruits, seeds, and foliage (Mulder-Krieger and Verpoorte 1994).

Molecular dynamics involved in the interaction of plant pigments with NPs have been successfully studied by biophysical, biochemical, biomolecular, and electrochemical behavior (Barazzouk et al. 2012; Mezacasa et al. 2020; Pontes et al. 2020; Bhogaita and Devaprakasam 2021). In general, these interactions were evaluated to understand: (*i*) the environmental implications of NMs, (*ii*) the physiological responses and biological phenomena, and (*iii*) to improve artificial photosynthesis and solar cells.

In this chapter, we discuss available data concerning engineered nanomaterials (ENMs) and their interaction with plant pigments in their biological properties. Contradictory results have been reported about the effects of NMs on different plant pigments. Detection techniques, possible in vivo implications, and side effects are discussed and an analysis of future research needs is also included.

5.2 Nanomaterial's Cellular Uptake and Intracellular Transport

Engineered nanomaterials are emerging as delivery vehicles for biomolecules in plants, especially for plant genetic transformation (Zhao et al. 2018), biostimulants (Juárez-Maldonado et al. 2019), fertilizers (Kopittke et al. 2019), and pesticides (Pontes et al. 2021). However, the incorporation and target of NMs in plants are challenging due to the presence of plant cell walls, differences in membrane chemical compositions compared to mammals' cells, and low endocytic rate (Miralles et al. 2012; Husen and Siddiqi 2014).

The first barrier that ENMs must overcome to entry the cell is the cell wall. Regardless of the organ of the plant (in leaf epidermis, for example, there is also a cuticle, a layer that covers the outer periclinal walls and is composed mainly of lipid substances).

Plant cell walls are mainly composed of cellulose, hemicelluloses and pectins, and a large number of proteins are involved in the cell dynamics through diverse functions such as environmental sensing, growth, signaling and defense (Fry 2004; Hijazi et al. 2014). For a long time, the cell wall was taken as a non-dynamic and functional limited structure, however, this view has changed drastically.

Some authors argue that the movement of molecules through the wall is limited by the pore size. The pore size is defined as the space between the cell wall components and the wall matrix (Salmén 2004; Rondeau-Mouro et al. 2008; Kurczynska et al. 2021). The cell wall pore size of several species has been documented e.g. *Chenopodium album* Linn. (Chenopodiaceae) in which the pore sizes vary from 3.3 to 6.2 nm, depending on experimental conditions (Fleischer et al. 1999). In *Achlya bisexualis* Coker & Couch (Saprolegniaceae) the pores in the wall were determined to be 2–3 nm (Money 1990). In *Hordeum vulgare* Linn. (Poaceae) roots the pore size of rhizodermal cell walls was 3.2–3.8 nm (Milewska-Hendel et al. 2017). This hypothesis seems unsupported and unlikely since much larger sized NPs were noticed within plant tissues, even when they contacted the outer wall. *Glycine max* Linn. merrill (Fabaceae) and *Medicago sativa* Linn. (Fabaceae) plants absorbed citric acid-coated magnetite Fe_3O_4NPs about 18 nm diameter. These particles accumulated in roots. Little or no translocation to the aerial parts was observed (Iannone et al. 2021). *Oryza sativa* Linn. (Poaceae) absorbed silver nanoparticles (AgNPs), with diameter varying from 20 to 150 nm (Thuesombat et al. 2014). Treatment of *Cucurbita pepo* Linn. (Cucurbitaceae) with superparamagnetic iron oxide NPs, about 12.5 nm in size, also showed that these particles pass the cell wall (Tombuloglu et al. 2019a, b). Moreover, it was shown that zinc oxide NP (ZnO-NP) of 8 nm in diameter may enter cytoplasm of root cells of *Brassica sp.* Linn. (Brassicaceae) species (Molnár et al. 2020). None of the works mentioned above explores the main question related to the passage of molecules through the cell wall: what mechanism allows NPs to cross the cell wall barrier?

Although the mechanisms of NMs passage through the cell wall are not yet completely understood, it is almost unanimous in the literature that the change in the chemical composition of the cell wall is involved in this process (Kurczynska et al. 2021). Such change, related to response to biotic and abiotic factors, are increasingly investigated as an adaptation mechanism to altering environmental conditions (Milewska-Hendel et al. 2017). Chemical composition of the cell wall influences its structure, including porosity. This parameter in turn determines the pore size of walls and controls the apoplastic exchange of macromolecules (Kurczynska et al. 2021). Recent studies also elucidated the cell wall as a dynamic structure during secretion passage on secretory structures (Miguel et al. 2006, 2017) and silver NPs passage (Paiva Pinheiro et al. 2021).

Until recently, the most accepted mechanism for the passage of NMs through cell walls involved the rupture due to NPs accumulation on the cell wall surface. Most

parts of these studies were conducted in the bacteria, fungi, and microalgae cell wall (Concha-Guerrero et al. 2014; Athie-García et al. 2018; Wang et al. 2019).

A detailed mechanism was proposed for the passage of AgNPs through the cell wall of *Lactuca sativa* var. crispa Linn. (Asteraceae) and occurs in three steps: AgNPs contacts the outer cell wall, presenting two states of oxidation, silver ion (Ag^+ and Ag^0); the interaction of oxygen with the Ag^+ leads the rupture of hydrogen bonds on cellulose microfibrils; hydrogen bonds break spaces large enough to AgNPs freely passage through the outer cell wall (Paiva Pinheiro et al. 2021). This work was the first to convincingly elucidate the mechanism of passage of AgNPs through the cell wall using *L. sativa* as a model. However, the surface chemistry of ENMs is also very important as it may influence NPs reactivity, penetration and movement within the plant and therefore plant responses to the same type of NPs may be completely different (Zhu et al. 2012; Wang et al. 2014; Li et al. 2016; Milewska-Hendel et al. 2019).

As discussed, it is likely that other plants exhibit peculiarities in the passage of metallic NPs through the cell wall, however, this mechanism seems quite attractive since it explains the process based on the behavior of cellulose microfibrils, common to all cell walls of higher plants. After crossing the entire cell wall barrier, before entering the cytoplasm, the nanostructured materials must pass through the cell membrane.

ENMs cellular uptake has been mainly studied in animal cells (see Zhao et al. 2011; Foroozandeh and Aziz 2018). Different endocytic pathways seem to be responsible for the internalization of these materials, however, these results cannot be used as models to plant cells, due to the presence of the cell wall, which became an additional barrier outside the plasma membrane (Palocci et al. 2017).

Plant uptake of ENMs is hardly predictable. It depends on multiple factors including the NP itself (size, chemical composition, net charge and surface functionalization); the application routes; and the interactions with environmental components (soil texture, water availability, microbiota) (Sanzari et al. 2019). In addition, anatomical and ultrastructural variations of each species must also be considered. Different plant cell membranes, e.g., plasmalemma and plasma membrane, are known for selective absorptivity and permit small nonpolar ions diffusion through the membrane (Ghorbanpour and Wani 2019). Larger and polar molecules such as water, ions, and other foreign particles (including ENMs) cannot easily diffuse across the phospholipid bilayer. Although this process is not simple, many ENMs are able to break through this barrier and enter the cell.

Several mechanisms have been proposed for ENMs uptake in plant cells, e.g., by endocytosis, binding to carrier proteins, through aquaporins, ion channels, creating new pores, or by binding to organic chemicals in the environmental media (Rico et al. 2011). The most investigated mechanism for cellular uptake of ENMs in plant cells is endocytosis. The internalization of ENMs depends on the interaction established with the plasma membrane and the type of endocytosis is associated with physicochemical characteristics of NMs (size, chemical composition, charge, surface functionalization, surface reactivity and surface adsorption) (Jiang et al. 2011). Endocytosis can be classified as phagocytosis, which involves the internalization of particles larger

than 1 µm and pinocytosis involves the internalization of particles smaller than 500 nm (Costa Verdera et al. 2017). Pinocytosis can further be classified as clathrin-mediated endocytosis (CME), caveolin-mediated endocytosis (CAV), macropinocytosis, clathrin-independent endocytosis (CIE) and caveolin-independent endocytosis (CIEV) (Yameen et al. 2014). CME was identified as the dominant endocytic process in plant cells and appears to operate analogously to animal cells (Surpin and Raikhel 2004). CME involves the formation of vesicles from the polymerization of the protein clathrin that acts as a transporter of several compounds to the cell across the plasma membrane and released into the cytoplasm (Costa Verdera et al. 2017). Studies show that the size limit of particles entering cells via CME has been reported to be around 200 nm (Rejman et al. 2004; McMahon and Boucrot 2011).

Caveolin-mediated endocytosis is another mechanism that transports NPs across the plasma membrane to the cell. These caveolae are membrane invaginations, enriched with cholesterol and sphingolipids (Lajoie and Nabi 2007). Several reports suggest that caveolae sizes limit the uptake of NPs larger than individual caveolae sizes (approximately 50–100 nm) (Wang et al. 2012; Akinc and Battaglia 2013).

Macropinocytosis involves the transport of large amounts of extracellular material through vesicles known as macropinosomes. Macropinosomes provide an effective pathway for endocytosis of macromolecules, as their structure is substantially larger with a diameter of 0.5–10 µm (Falcone et al. 2006). Clathrin and caveolin-independent endocytosis do not use the classic routes of internalization, but they are responsible for the transport of large amounts of extracellular material. A CIE and CAIE do not require the presence of coat proteins for the formation of vesicles and internalization of extracellular material (Sandvig et al. 2008). Most of studies on plant endocytosis were performed in suspension cells, which do not recapitulate tissue structure and have been reported to possess half-plasmodesmata that expose the cell membrane to the extracellular environment (Bayer et al. 2004). For these reasons, information about this topic must be taken with care. When crossing the cell membrane, NPs are transported to the cell target by several mechanisms.

Once in the cytoplasm, cell to cell movements of ENMs are facilitated by plasmodesmata, membrane-lined cytoplasmic bridges with a flexible diameter that ensure membrane and cytoplasmic continuity among cells throughout plant tissues. Transport of ENMs with variable sizes through plasmodesmata has been described in *Oryza sativa* (Lin et al. 2009), and poplar plant species (Zhao et al. 2017). Through the symplastic and apoplastic pathways, small particles can reach the xylem and phloem vessels and translocate in the whole plant to different tissues and organs. Remarkably, organs like flowers, fruits and seeds normally have a strong capability to import fluids from the phloem (sink activity) and tend to accumulate NMs.

In the cell, the address of these NMs is directly related to their characteristics such as size, charge, and pH. According to the characteristic of the ENMs they are endocytosed by different pathways (Jiang et al. 2011). After entering the cell, the ENMs acquire lipoprotein coverage (Sahay et al. 2010) and follow the classic route that begins with the fusion of ENMs with early endosome, then it becomes a late endosome and finally the transfer of the material to the lysosomes (Lab and Jesus 2014). Until reaching lysosomes, NMs go through several maturation processes and

decrease their pH and this traffic is regulated by RAB proteins (Family G-proteins) (Yameen et al. 2014).

ENMs can follow an alternative route, a fact related to their characteristics and hence the importance of characterizing these ENMs. The most usual alternative to scape endosomal degradation is related to the alteration of the NPs surface charge, the surface functionalization of NPs with an amine (Ogris et al. 2001). The fate of NPs in the cell can be in a specific way with surface functionalization or in a non-specific way for different organelles such as the nucleus, Golgi apparatus, mitochondria and endoplasmic reticulum (Yameen et al. 2014). An accurate analysis regarding ENMs plant interactions concern not only the degree of toxicity of ENMs on living organisms, but also detailed studies of their uptake and movement within the plant body on different levels of organization: organs, tissues and cells (Kurczynska et al. 2021). These ENMs are transported via apoplast to the endodermis and via symplast to the vascular system (Pariona et al. 2017). Xylem is the most significant carrier in the dissemination and transfer of ENMs (Aslani et al. 2014) and studies show the rapid absorption of NPs through conductive vessels.

A study with different crop plants showed that after 24 h of exposure of the root to bioferrofluid (magnetic carbon-coated NPs), the NPs were able to leak into vascular tissues and reach the aerial parts of the plants (Cifuentes et al. 2010). In another study, it was observed that iron NPs (IO-NPs) were absorbed by the roots of maize seedlings and through the vascular system reached the shoot and accumulated in the leaves (Pariona et al. 2017). A similar result was observed by Tombuloglu et al. (2019a) in barley plants.

Furthermore, the translocation of NPs can occur in the reverse way, from phloem to xylem. González-Melendi et al. (2008) showed that the translocation of NPs applied in the aerial part of plants went to the roots and there is evidence that cell–cell transport occurs (Corredor et al. 2009) which may involve the traffic path through the plasmodesmata (Cifuentes et al. 2010). A similar result was observed by Wang et al. (2012) in which copper NPs (CuONPs) were found in the xylem of maize seedlings, indicating xylem-mediated transfer of NPs from root to shoot. In addition, reverse movement through the phloem.

Although osmotic pressure favors the uptake and translocation of NPs, the NPs can accumulate in the root and not be translocated throughout the plant (Iannone et al. 2016). As mentioned earlier, absorption, endocytosis and translocation will depend on the characteristics of the ENMs and the type of plant species used in the study. Figure 5.1 shown a schematic representation of uptake and traffic of ENMs on plant cells.
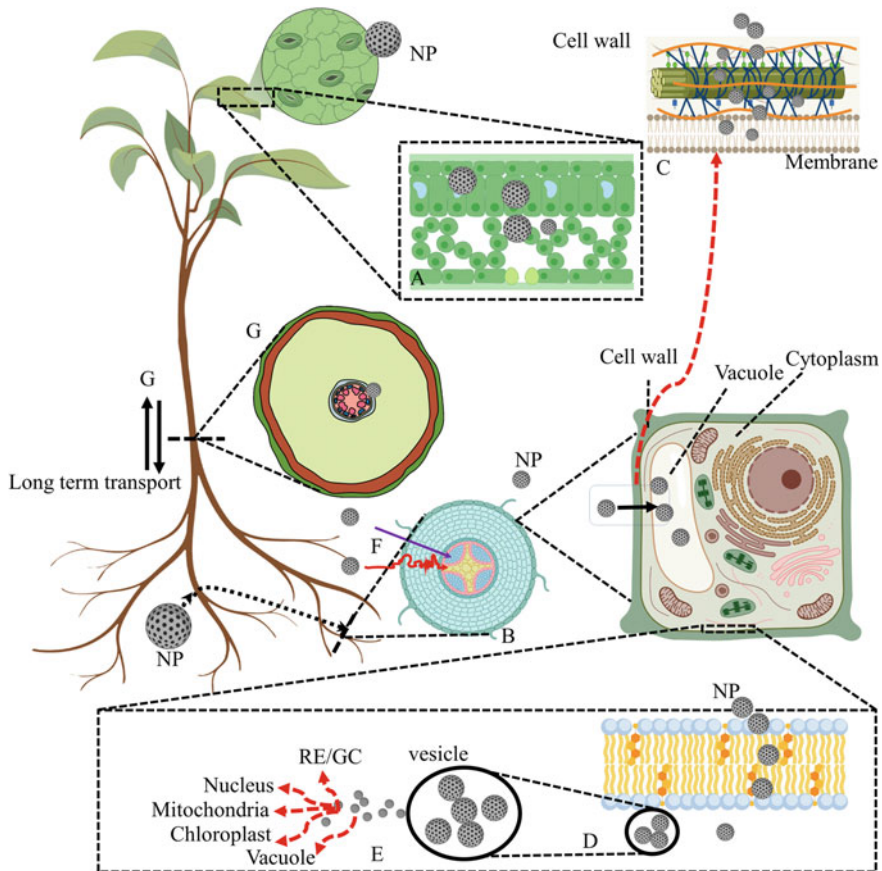
Fig. 5.1 Schematic representation of ENMs uptake and traffic on plant cells. ENMs contact plants in different ways. The nanostructured material can come into contact through the leaf (**a**) or root (**b**). Regardless of the contact route, the first barrier that must be overcome for the internalization of NMs in the cell wall (**c**). Then, to enter the symplast pathway, it is necessary to pass through the cell membrane (**d**). Subsequently, ENMs can be delivered to different organelles, either by vesicles or free in the cytoplasm (**e**). Sometimes the particles continue their apoplast movement until they reach the endoderm and pericycle, are forced into the symplast pathway reaching the xylem and phloem cells (**f**). If this happens, long term transport through vascular tissue (**g**) may be possible. The sequence of events, from the interaction between NMs and cell walls to long term transport, is a particular result of the interaction of each particle and plant, in addition to the concentration and route of exposure. Therefore, these results are unpredictable most of the time. A and B– ENMs contact to cell wall; C—Accumulation and passage through the cell wall; D—Passage through the cell membrane; E—Transport, traffic and targeting; F—Apoplast transport and G—Long distance transport. (Figure constructed by the authors)

5.3 How Do Nanomaterials Interacts with Photosynthetic Pigments?

For photoautotrophic organisms, physiological and/or ecological functions, such as energy absorption, antioxidant activity, protective or reproductive processes, and some others, are related to a large range of molecules categorized as pigments. The most important contribution of natural pigments is related to Earth's biosphere maintenance due to their role in the water-splitting activity responsible for oxygen photodissociation.

Photosynthesis (from Greek photo → light and synthesis → putting together) is one of the most important processes on Earth and spawns a research field that is intrinsically interdisciplinary. From ancient environments (ca. 2.8–2.4 billion years ago), when the first oxygenic cyanobacteria began to utilize the photosynthetic process until the evolution of land-based plants, the driving selective forces acted to oxidize the water molecule and fix carbon in high amounts (Melkozernov 2014; Stirbet et al 2014). As a consequence of their organic evolution, some molecules with phenotype chromophore properties were promoted by natural selection, i.e., compounds with high absorption at the visible portion of the electromagnetic spectrum.

In oxygenic photosynthesis of higher plants, electrons are extracted from water by solar energy (photons) absorption followed by their incorporation into CO_2 to synthesize organic compounds, such as sugars, as storable chemical energy ($NADPH^+$ and ATP).

Chloroplasts (Fig. 5.2) are bioenergetic plant cell organelles of diameter 5–10 μm. These structures are responsible for photosynthesis, with each plant cell, mainly leaves, containing about 10–100 chloroplasts (Cooper 2013). Chloroplasts comprise two membranes: an outer membrane that delimits the organelle and an inner membrane related to inner functions. Between the outer and inner membrane, a space of 10–20 nm defines its intermembrane space. In the inner organelle portion is the chloroplast stroma, a soluble matrix of dense fluid and an internal membrane system of layered thylakoids, called "grana" (Cooper 2013).

Pigments are the part of the macromolecular structures that absorbs light in the visible region of the spectrum (Walsby 1974). A large range of pigments can be found in different photosynthetic organisms such as chlorophylls (Chl) *a–f*, carotenoids (Car), bacteriochlorophylls (B-Chl) *a–g*, and bilins (phycoerythrin, phycocyanin, and allophycocyanin).

In summary, Chl-*a* molecules are primarily responsible for photochemical reactions. ENMs can interact differently with these and other plant pigments according to their physical–chemical properties and pigment type, resulting in two basic responses: changes in the pigment content (increase/decrease) by induction of the pigment synthesis or its inhibition and/or degradation and changes in the pigment activities, especially light absorption and energy dissipation processes such as the behavior of fluorescence emission, electron transport, and others related to non-photochemical quenching. In general, when plants are exposed to NPs, the most
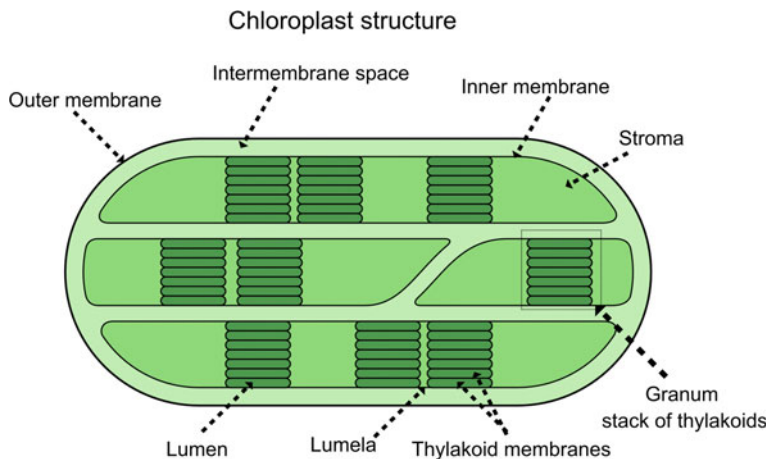
Chloroplast structure

Fig. 5.2 Schematic representation of chloroplast structure. Chloroplasts are semiautonomous organelles in plants, algae, and cyanobacteria cells. Light energy is transduced into chemical energy at the thylakoid membrane, and the fixation of CO_2 takes place in the stroma side. (Figure constructed by the authors)

significant effect described in the literature is the reduction of chlorophyll content followed by an increment in the amount of accessory pigments (Table 5.1).

5.3.1 Chlorophyll and Derivatives

Chlorophyll (Chl) pigment is a green-colored, lipid-soluble porphyrin derivative with magnesium (Mg) as the central atom; it is found in all photoautotrophic organisms (Mulder-Krieger and Verpoorte 1994; Cooper 2013; Kuczynska et al. 2015). The chlorophylls are located into chloroplast organelles and play a crucial role in photosynthetic light reactions. A wide range of chlorophyll forms (*a–f*) can be found in different photosynthetic organisms, depending on their functional groups (methyl, ethyl, formyl, vinyl). Chlorophyll-*a* and chlorophyll-*b* molecules (Fig. 5.3) are primarily responsible for photochemical reactions in higher plants.

In the last decades, it has become increasingly interesting to understand the interaction of ENMs and photosynthetic pigments for environmental impact monitoring purposes or for the development of novel materials for artificial photosynthesis. For instance, changes in pigment activities have been described as variations on the excited-state of chlorophyll-a interacting with gold NPs (AuNPs) (Barazzouk et al. 2012; Falco et al. 2011; Torres et al. 2018; Mezacasa et al. 2020).

Under excitation energy (blue and red light around 680 nm and 760 nm, respectively), the chlorophyll molecule may oscillate between different energy states, with electronic transitions from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) (Müh and Renger 2014), dissipating part

Table 5.1 Effects in the pigment content of plants exposed to nano-metal particles

NP	Size (nm)	Organism	Pigment content decrease	Pigment content increase	Refs.
Silver (Ag)	20	*Arabidopsis thaliana* Linn. Heynh (Brassicaceae)	Chl (total)	Anthocyanin	Nair and Chung (2014)
	2–11	*Brassica rapa* Linn. (Brassicaceae)	Chl (total)	Anthocyanin	Thiruvengadam et al. (2015)
	23 ± 4	*Chrysanthemum grandiflorum* Ramat. (Asteraceae)	n.a	Carotenoids	Tymoszuk and Kulus (2020)
	10–30	*Lactuca sativa* Linn. var. foliosa (Asteraceae)	n.a	Carotenoids, and increase Chl *a* content	Jurkow et al. (2020)
	100	*Stevia rebaudiana* Bertoni (Asteraceae)	n.a	Anthocyanin and Chl (total)	Ramezani et al. (2019)
	58–80	*Viola tricolor* Linn. (Violaceae)	n.a	Rutin, Luteolin, Apigenine, and Quercetin	Hassanvand et al. (2021)
	14	*Withania coagulans* Stocks (Solanaceae)	Anthocyanin—dose dependent	Chlo *b*, and Carotenoids—dose dependente	Tripathi et al. (2020)
	10	*Wolffia globosa* den Hartog & van der Plas (Araceae)	Chlo *a* and Carotenoids	n.a	Zou et al. (2016)
Arsenic trioxide (As$_2$O$_3$)	20	*Hordeum vulgare* Linn. (Poaceae)	Chl (total)	Anthocyanin and Carotenoids	Selim et al. (2021)
	20	*Zea mays* Linn. (Poaceae)	Chl (total)	Flavonoids	Selim et al. (2021)
Gold (Au)	5–30	*Chlorella zofingiensis* Linn. (Chlorophyceae)	n.a	Carotenoids	Li et al. (2020)

(continued)

Table 5.1 (continued)

NP	Size (nm)	Organism	Pigment content decrease	Pigment content increase	Refs.
	10–30	*Lactuca sativa* Linn. var. foliosa (Asteraceae)	n.a	Carotenoids	Jurkow et al. (2020)
Cerium oxide (CeO_2)	8	*Phaseolus vulgaris* var. Red Hawk Linn. (Fabaceae)	Chl *a* and Carotenoids	n.a	Majumdar et al. (2016)
	130	*Salvinia auriculata* Aubl. (Salviniaceae)	Chl (total)	Carotenoids	Pontes et al. (2019)
Copper oxide (CuO)	25–55	*Brassica rapa* var. rapa Linn. (Brassicaceae)	Chl (total) and Carotenoids	Anthocyanin	Chung et al. (2019)
	120	*Lemna valdiviana* Phil. (Lemnaceae)	Chl *a*	n.a	Pontes et al. (2020)
	50	*Oryza sativa* Linn. (Poaceae)	Chl (total) and Carotenoids	n.a	Yang et al. (2020)
	25–55	*Solanum melongena* Linn. (Solanaceae)	Chl (total)	Anthocyanin and Flavonoids—dose- dependent	Baskar et al. (2018)
	30–40	*Zea mays* Linn. (Poaceae)	Carotenoids	Anthocyanin and Chl (total)	Nguyen et al. (2021)
Iron oxide (Fe_2O_3)	100	*Trachyspermum ammi* Linn. (Apiaceae)	Chl *a*	Anthocyanin, Carotenoids and Chl *b*	Abdoli et al. (2020)
Nikel (Ni)	10 - 20	*Solanum melongena* Linn. (Solanaceae)	Chl (total)	Anthocyanin and Flavonoids—dose- dependent	Baskar et al. (2018)
Silicon oxide (SiO_2)	10–20	*Scenedesmus obliquus* (Turpin) Kuetzing. (Scenedesmaceae)	Chl (total)	n.a	Wey et al. (2010)

(continued)

Table 5.1 (continued)

NP	Size (nm)	Organism	Pigment content decrease	Pigment content increase	Refs.
Platinum (Pt)	10–30	*Lactuca sativa* L. var. foliosa (Asteraceae)	n.a	Carotenoids	Jurkow et al. (2020)
Titanium oxide (TiO$_2$)	10–30	*Lycopersicum esculentum* Mill (Solanaceae)	Chl (total)	Anthocyanin Carotenoids	Ko and Hwang (2019)
Zinc oxide (ZnO)	30	*Carex vulpina* Linn. (Cyperaceae)	Chl (total), Neoxanthin and Lutein	β-carotene, Violaxanthin and Zeaxanthin	Haisel et al. (2019)
	18	*Solanum melongena* Linn. (Solanaceae)	Chl (total)	Anthocyanin and Flavonoids—dose—dependent	Baskar et al. (2018)

n.a. = not applicable
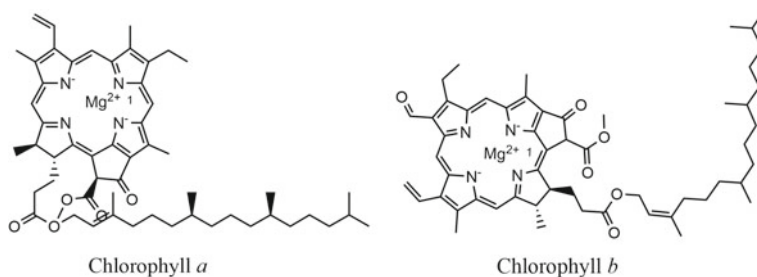
Fig. 5.3 Chlorophyll *a* and *b* structures with a magnesium as the central atom. (Figure constructed by the authors)

of the primary absorbed energy to the electron transport chain (photochemical process) and another part via the non-photochemical or quenching process (heat and fluorescence) (Roháček 2002; Ashraf and Harris 2013).

Nanoparticles can interfere with the regular behavior of chlorophyll, reducing its fluorescence dissipation. This occurs either via a static process, i.e., interaction with the fluorophore molecule (chlorophyll) to form a non-fluorescent complex or via dynamic processes, i.e., when the NPs acting as a quencher, reducing the fluorescence intensity by fluorophore deactivation; this suppression is directly related to particle size and is dose-dependent (Acquavella et al. 1995; Sharma et al. 2019; Damera et al. 2020). On the other hand, up-converting and down-converting NPs were able to transform infrared light into visible light or ultraviolet light into visible light, respectively (Yanykin et al. 2022). These NPs can be exploited to improve photosynthesis.

In general, AuNPs suppress the electron transfer process from excited chlorophyll molecules. Additionally, the photodegradation behavior of Chl-a can be slowed during its interaction with AuNPs (Barazzouk et al. 2012) and this information provides important insight for the development of efficient hybrid artificial photosynthesis. Interaction between chlorophyll and silver NPs (AgNPs) was investigated by Falco et al. (2015) and Queiroz et al. (2016), who showed that AgNPs can disrupt photosynthetic electron transport via excited electron transfer from the chlorophyll molecules to the AgNPs surface (Fig. 5.4). Additionally, this behavior was dependent on NPs size and concentration.

Recently, the temperature-dependent interaction behavior of chlorophyll with zinc oxide, copper oxide, titanium dioxide, and iron oxide NPs was studied (Sharma et al. 2019, 2020). These studies also observed that electrons can be relocated from the excited chlorophyll to the conduction band of the surface of the NP. However, the authors suggest that with the temperature increase, hydrogen bonding and van der Waals forces are the prominent driving forces during this interaction, and this process is spontaneous and exothermic.

Under in vivo cellular media, chlorophyll molecules are susceptible to losses of their Mg atom (magnesium dechalatase) due to low pH or heat conditions. This reaction is called "pheophytinization" and results in pheophytin formation when two
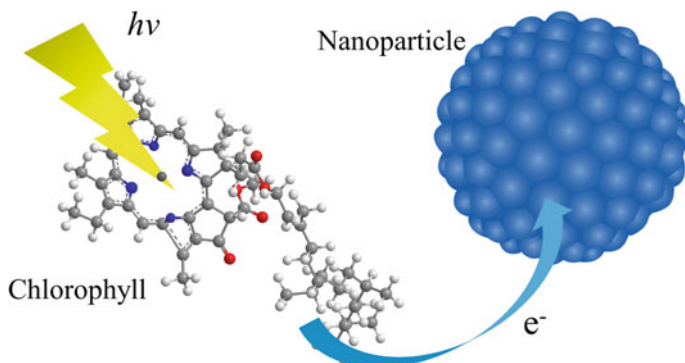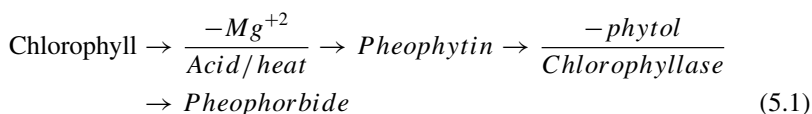
Fig. 5.4 Schematic representation of excited electron transfer from chlorophyll molecule to nanoparticle surface. *hv*: is the energy of a photon, and e⁻: is the excited electron. (Figure constructed by the authors)

hydrogen ions replace the Mg ion found in the center of the porphyrin ring (Sato et al. 2018). Pheophytin plays a key role in Photosystem II (PSII) electron transport. Structurally, D1 and D2 proteins contain special chlorophyll P680, chlorophyll-a, and pheophytin in the reaction center of PSII (Santiago et al. 2020; Pontes et al. 2020). Chlorophyllase enzyme may be binding with the phytyl group of pheophytin, resulting in pheophorbide formation. Equation 1 summarizes the formation of chlorophyll derivatives [Eq. 1]. Size dependence was studied using in vitro and theoretical experiments to understand the interaction of AuNPs and pheophytin (Mezacasa et al. 2020). The interaction mechanisms reported for pheophytin and pheophorbide molecules are also similar to chlorophyll via photoinduced electron transfer from pheophytin or pheophorbide molecules to AuNPs surface (Mezacasa et al. 2020; Kotkowiak and Dudkowiak 2015).

$$Chlorophyll \rightarrow \frac{-Mg^{+2}}{Acid/heat} \rightarrow Pheophytin \rightarrow \frac{-phytol}{Chlorophyllase}$$
$$\rightarrow Pheophorbide \tag{5.1}$$

The impact of the nanomaterial's interaction on plant photosynthetic pigments, particularly with chlorophyll and its derivates, may alter the cellular homeostasis, metabolism, physiology, and the plant life cycle. Consequently, this either positively or negatively modifies plant productivity.

5.3.2   Carotenoids

Carotenoids (Car) are a class of natural pigments with important roles in biological systems. In photosynthesis, Car act as accessory light-harvesting pigments and can efficiently transfer absorbed light energy to chlorophyll molecules (Zulfiqar et al. 2021). Additionally, another important role of the Car at the thylakoid membranes during photochemistry is photoprotection by dissipating excess energy to the environment (Collini 2019). In general, carotenoids can be divided into two major groups based on their chemical structure: cyclic hydrocarbons (carotenes) and hydrocarbons containing oxygen (xanthophylls) (Jan and Abbas 2018).

The interaction of NPs with carotenoids may be affected by several factors related to the nature of the nanoparticle, the type of carotenoid molecule, and the interaction of the NMs with the cellular environment (Santiago et al. 2020; Miguel et al. 2021). For instance, Heisel et al. (2019) report an increase in negative effects of cadmium contamination in *Carex vulpina* Linn. (Cyperaceae) plants exposed to ZnO NPs. These authors observed a strong decrease in the neoxanthin and lutein content, suggesting damages to light-harvesting complexes, also, increased β-carotene content suggests stress behavior.

Once the NPs penetrate the plant chloroplast and interact with carotenoids, complexation of the nanomaterial and pigment may occur. For instance, the strong complexation of carotenoids containing terminal carboxyl groups (-COOH) with the TiO_2 surface leads to electron transfer from the adsorbed carotenoid molecule to the surface trapping site (Wang et al. 2005). Carboxyl groups enhance the binding of carotenoids onto the surface of TiO_2 NPs. This strong attachment can effectively facilitate electron transport from excited carotenoids by injecting electrons from their excited states into the conduction band of TiO_2 NPs (Wang et al. 2005). Additionally, photosensitization of the TiO_2 NPs with β-Carotene, 8′-apo-β-carotene-8′-al, and canthaxanthin leads to the formation of superoxide anion (O_2^-) and singlet oxygen ($^1O_2$) on red light irradiation (Konovalova et al. 2004) as schematized in Fig. 5.5.

On the other hand, according to nanoparticle size, AuNPs may act as light-harvesting NPs and demonstrate the enhanced biosynthesis of carotenoids — 42.7% higher than without light-harvesting gold NPs (Li et al. 2020). In vivo studies have shown that the characteristics and nature of the NMs, in addition to the environmental factors, will greatly influence the synthesis and accumulation of carotenoids in plant tissues (Zou et al. 2016; Manjudar et al. 2016; Pontes et al, 2020). According to Pan et al. (2004), carotenoids with pheophytin molecules in contact with metal oxide NPs may form a self-assembled system, leading to an efficient reductive quenching of the pheophytin moiety. This result suggests that a similar mechanism can operate also in natural photosynthetic systems. Additionally, the impact of NMs' interaction on carotenoids pigments may alter the plant physiological responses (Boonlao et al. 2022). At the reaction center, carotenoids can play the role of electron donor when a suitable electron acceptor is available. They can also effectively quench chlorophyll
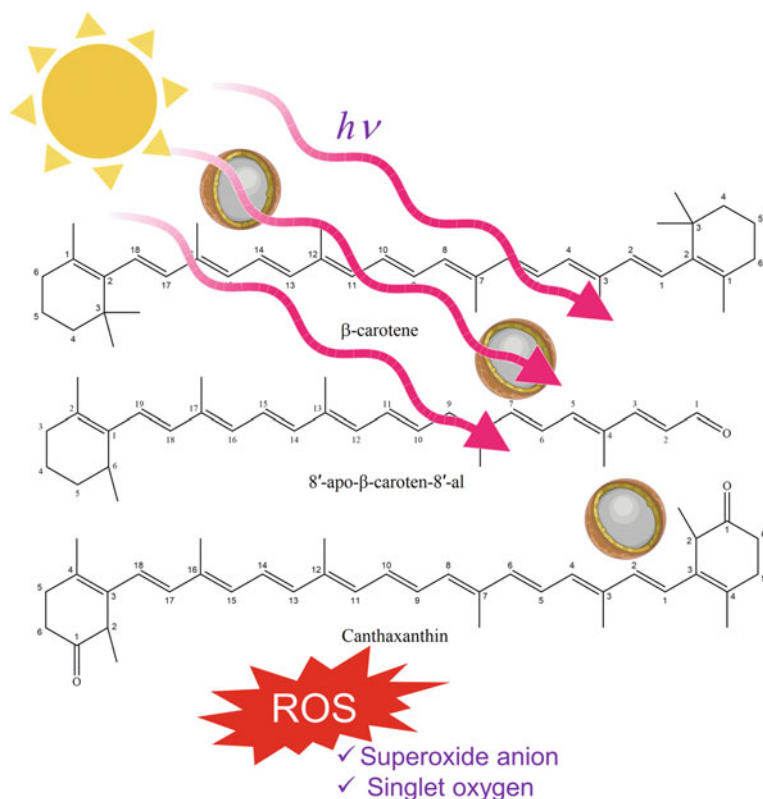
Fig. 5.5 Generation of superoxide anion and singlet oxygen in irradiated TiO$_2$ nanoparticles during its interaction with carotenoids. *hv*: is the energy of a photon. (Figure constructed by the authors)

triplet states and the formed triplet states of carotenoids can harmlessly dissipate the excess energy to the environment.

Despite many studies conducted experimentally with several plant model organisms on nanomaterial exposure, the disparity in results between physiological and molecular in vivo studies is remarkable (Santiago et al. 2020; Costa-Ruiz et al. 2021). Even if nano-enabled agriculture or artificial solar cells technologies show us success stories in the areas cited above, these new areas still have major challenges and limitations that must be overcome to achieve the desired outcome, particularly in terms of the interaction between NMs and non-chlorophyll pigments.

5.4 Anthocyanins

Anthocyanins are a class of natural red pigments present in leaves, petals, stamens, tuberous roots, and particularly in vacuoles of red-colored epidermis cells (Fang, 2014). Anthocyanins act as a cell protection agent and are considered antioxidant molecules (Gould et al. 2002). Biotic and abiotic stress, such as herbivory, high temperatures, and ultraviolet radiation, can trigger changes in anthocyanin content (Hatier and Gould, 2009), and can induce the generation of reactive oxygen species (ROS) in the plant cells. Consequently, increases the expression of MYB, basic helix-loop-helix (bHLH), and WD40 genes involved in the anthocyanin biosynthesis pathway (Tahara, 2007).

The interaction between NMs and anthocyanins may occur on isolated compounds (in vitro assays) and/or at a cellular/biochemical level as described by Ravanfar et al. (2016) who has researched solid lipid NPs as carriers for anthocyanins. A recent study by Amin et al. (2017) demonstrated that anthocyanins loaded onto polyethylene glycol (PEG) nanocapsules can decrease oxidative stress on the p38/c-Jun N-terminal kinases (JNK) pathway of SH-SY5Y cells. In general, the extraction methods for anthocyanin usually require complex enzymatic procedures of extraction and higher costs, and are time-consuming. On the other hand, nanobiocatalysis using nanomaterial functionalized with α-amylase demonstrated a higher efficiency for anthocyanin extraction (Yi et al. 2021). For instance, after NP internalization in biological systems, the nanomaterial directly interacts with reactive molecules (Miguel et al. 2021). In *Arabidopsis* leaves, TiO_2 NPs can induce cell membrane damage and anthocyanin capping the surface of TiO_2NPs, forming a pigment-layer, which is responsible for the blue color of internalized NPs (Kupera et al. 2020).

Another factor that has an impact on nanoparticle–anthocyanin interaction is the synthesis route of the nanomaterial and the anthocyanin synthesis pathway (Fig. 5.6). According to Ramezani et al. (2019), nanosilver synthesized via the green route using *Stevia rebaudiana* Bertoni (Asteraceae) extracts increased the synthesis of anthocyanin when compared with chemically synthesized nanosilver. On the other hand, Tripathi et al. (2020) revealed a dose-dependent decrease in anthocyanin content in *Withania coagulans* Stocks. (Solanaceae) in response to biogenic nanosilver. Hassanvand et al. (2021) reported increased gene expression of flavonoid biosynthesis pathway via phenylalanine ammonia-lyase (PAL) and chalcone synthase (CHS) genes. In this study, Hassanvand and co-workers, using *Viola tricolor* Linn. (Violaceae) plants exposed to AgNPs, also observed an increase in the content of anthocyanin. This finding corroborates with the increase observed in the activity of phenylalanine ammonia-lyase and flavonol synthase enzymes in *Brassica rapa* Linn. (Brassicaceae) plants exposed to CuO NPs (Chung et al. 2019). Additionally, *Chrysanthemum grandiflorum* Ramat. (Asteraceae) inflorescence colors are affected by silver NPs due to alterations to gene expression; hence, changes in anthocyanin amount are responsible for the phenotypic response (Tymoszuk and Kulus 2020).

Nano-enabled agrochemicals have shown prominence in the modern agri-food sector; hence it has become important to understand the metabolic interaction at the
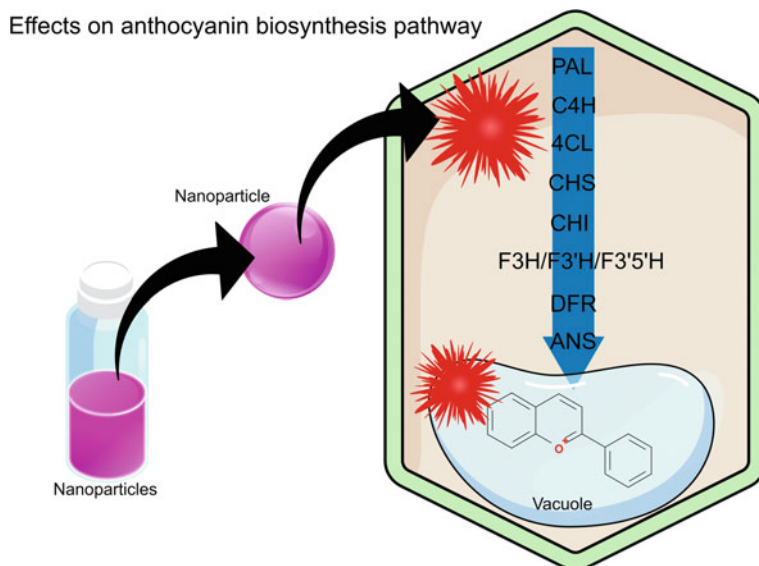
Fig. 5.6 Impact of engineered nanomaterials on the anthocyanin biosynthesis pathway. PAL: phenylalanine ammonia lyase; C4H: cinnamate 4-hydroxylase; CHS: chalcone synthase; CHI: chalcone isomerase; F3H/F3'H/F3′5'H: flavanone-hydroxylases; DFR: dihy- droflavonol 4-reductase; and ANS: anthocyanidin synthase. (Figure constructed by the authors)

interface between NMs and plant pigments. With regard to secondary metabolism in plants, special attention has been given to flavonoids such as anthocyanins, especially changes in these pigment levels, which provide a reliable tool to evaluate the plant response to engineered NMs. Soybean plants under hydric stress and nanosized copper particles show an increase in anthocyanin production due to ROS response (Nguyen et al. 2021). These results suggest that CuONPs may alleviate hydric stress in soybean plants. In *Solanum melongena* Linn. (Solanaceae) plants exposed to metal oxide NPs, the anthocyanin amount increases with NPs uptake by plants (Baskar et al. 2018). Nanosilver exposure increased the anthocyanin content in *Brassica rapa* Linn. (Brassicaceae) (Thiruvengadam et al. 2015) and gold NPs also increased the anthocyanin content in *Arabidopsis* plants (Nair and Chung 2014). This behavior occurs probably due to the ROS generation induced by NPs exposure (Santiago et al. 2020).

Photosynthetic groups of C3 and C4 plants respond differently to environmental fluctuations. For instance, under the high availability of CO_2, plants tend to increase their anthocyanin content as an antioxidant molecule. In co-exposure of CO_2 with AS_2O_3 NPs on the C3 plant *Hordeum vulgare* Linn. (Poaceae), Selim and co-workers (2021) demonstrated an accumulation of anthocyanin in C3 plants in contrast with C4 plants *Zea mays* Linn. (Poaceae) that show low content of its pigment. In Pb-contaminated soils, silicon NPs regulate the anthocyanin amount in *Coriandrum sativum* Linn. (Apiaceae) plants in soils with elevated Pb levels (Fatemi et al.

2021). Also, exposure of *Trachyspermum ammi* Linn. (Apiaceae) plants to iron NPs improves the anthocyanin content under salinity stress (Abdoli et al. 2020). Another synergic behavior against salinity stress was observed by Gohari et al. (2021). Using carbon quantum dots in *Vitis vinifera* Linn. (Vitaceae) plants, these authors observed a decrease in anthocyanin content, probably due to changes in its biosynthesis pathway. Finally, the application of anthocyanin for dye-sensitized solar cells (DSSCs) has shown promising potential. For instance, DSSCs made from blackberry-based anthocyanin-capped TiO_2 NPs to give the largest photovoltaic output and this photovoltaic output compares well with silicon-based solar cells due to its high efficiency (Cramer et al. 2011).

5.5 Betalains

The betalains is another important and interesting group of water-soluble nitrogenous plant pigments and have been studied by photoelectrochemical assays (Zhang et al. 2008; Gandia-Herrero and Garcia-Carmona 2013). Particularly important is their interaction with engineered semiconductor NMs to design novel dye-sensitized solar cells, due to their eco-friendly and low cost of production. Betalains are divided into two classes: yellow betaxanthins and red–violet betacyanins (Zhang et al. 2008). Additionally, betalain pigments show higher pH-dependent redox properties.

According to Wendel et al. (2017), betalains show limited sunlight energy conversion efficiency for applications in environmentally friendly dye-sensitized solar cells (DSSCs). This insufficient electron injection quantum yield is the major reason for these phenomena. On the other hand, some studies reveal that the interaction of ENMs improves their sunlight energy conversion efficiency. For instance, a DSSC prepared with betalains adsorbed onto Ag and TiO_2 nanostructure surfaces yielded a better plasmonic-enhanced DSSC, giving a short-circuit current density (Jsc), fill factor (FF), and power conversion efficiency (PCE). In general, these modified DSSCs increase efficiency by 50% over the reference DSSC (Isah et al. 2016).

The role and relevance of betalains' light emission in flowers and fruits in attracting pollinators and/or seed dispersers is a matter of current ecological and biophysical debate (Gracía-Plazaola et al. 2015; Mori et al. 2018; Guerrero-Rubio et al. 2019). For instance, nanosilver has a phytostimulatory effect on flowering (Salachna et al. 2019). However, knowledge of the interaction of NMs with flower pigments and their pollinators is needed to better understand their ecological impact (Hooven et al. 2019).

In general, under natural environments, for seeds to grow and develop into new plants, they must be dispersed. The possible influence of ENMs on the fluorescence of betalains in seed dispersal may have biological relevance and needs to be investigated in further studies. For instance, quinoa grains contain a significant amount of betaxanthins and their levels can affect the vigor of the seeds (Escribano et al. 2017; Guerrero-Rubio et al. 2019). Thus, the discussion about the effects of NMs on

fluorescence and colors of seeds opens up to include a possible biological effect of nanostructures on these signals and, consequently, on seed dispersal behavior.

Consequently, the interaction mechanisms of nano-based materials with betalains can and will play an important role in the future of artificial photosynthesis, thus requiring a better understanding of their ecological safety (Fig. 5.7).
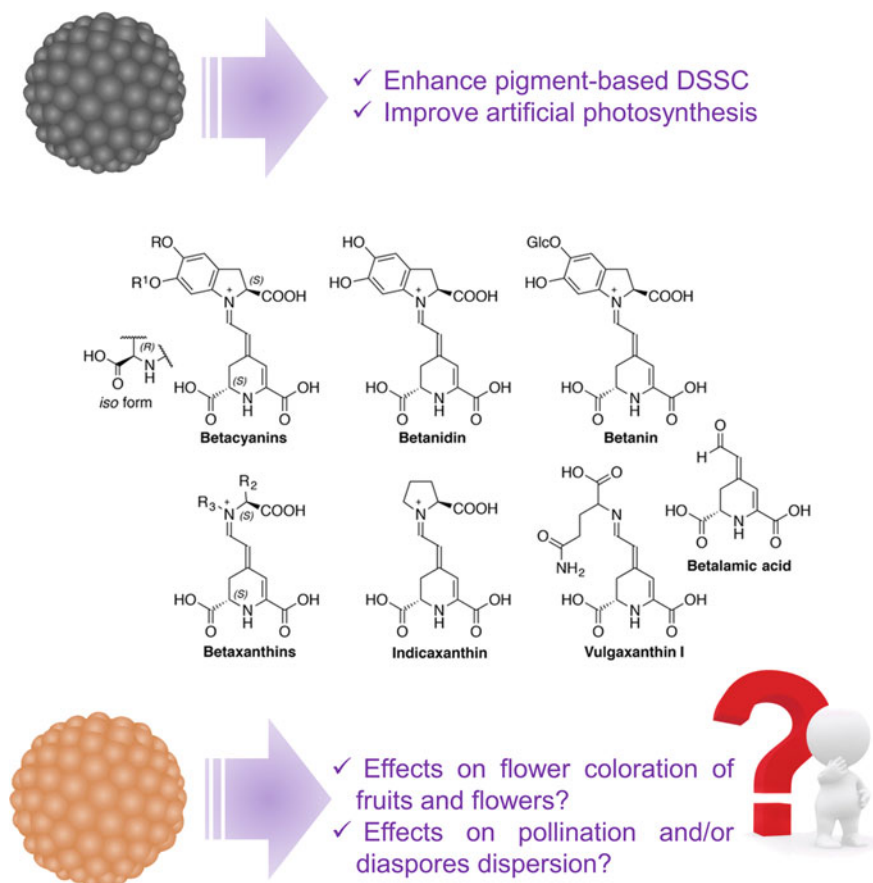

Fig. 5.7 Generic structures of betacyanins and betaxanthins, their biosynthetic precursor betalamic acid and several examples of naturally occurring betalains. Potential positive applications and negative side effects of the interaction of nanomaterials with betalains. (Figure constructed by the authors)

5.6 Optical and Spectroscopic Behavior of Nanomaterials-Pigment Interaction

Electromagnetic radiation is usually divided into γ-rays, x-rays (Roentgen waves), ultraviolet light, visible light, infrared, microwaves, and radio waves. All of these forms propagate as transverse electromagnetic waves with the same speed (speed of light, $c = 2.99792458 \times 10^8$ ms^{-1}) in a vacuum (Solè et al., 2005). The differences observed in the electromagnetic spectrum are related to wavelength and frequency (Skoog et al. 1996; Solé et al. 2005). Monochromatic electromagnetic radiation is commonly labeled by interrelated magnitudes: frequency (ν), wavelength (λ), wavenumber (ῡ), and energy of the photon (E), correlated as follows:

$$E = \frac{h}{v}$$

where h is Planck's constant (6.62×10^{-34} J.s).

In terms of wavelength and wavenumber.

$$E = \frac{h}{\lambda} = hc\bar{v}$$

where h is Planck's constant (6.62×10^{-34} J.s).

The wavenumber as well as the frequency is directly proportional to the energy. Electromagnetic radiation is made up of packets of energy called "photons" or "quanta." During interactions between radiation and matter, molecules in the lowest energy state (ground state) can have this condition changed commonly by absorption, transmission, and/or reflection of part of the absorbed radiation (Lehmann 2016).

The optical or spectroscopic properties of plant pigments during their interaction with ENMs depend on the arrangement between the nanostructure and the pigment molecule. A wide range of analytical methods is used to study the nanoparticle–pigment interaction behavior, particularly with optical interactions. These techniques require low cost and easy management, and fewer time-consuming processes (Lehmann 2016; Santos et al. 2021, 2022; Souza et al. 2022).

Absorption and emission behavior have been reported when plant pigment interacts with NPs because these pigments act as chromophores. For instance, AuNPs with sizes of 5 nm, 10 nm, and 20 nm induce a fluorescence quenching behavior in chlorophyll pigments (Falco et al. 2011). These effects were also related to the decrease in NPs size. These phenomena are correlated to photo-induced electron transfer from excited pigment molecules to the nanoparticle's surface. Similar results are observed with AgNPs by Queiroz et al. (2016). In this way, plasmonically generated changes in the absorption and emission behavior of pigments are reported due to the unique optical properties of metal NPs. These properties can be tuned by modifications of the size, shape, and chemical composition of the metal NPs. In another study, Brecht and co-authors (Brecht et al. 2012) used single-molecule spectroscopy to investigate the

plasmonic interaction effects of nanometer-sized hexagonal arrays of Au- and Ag-triangles on the fluorescence properties of chlorophyll pigments onto Photosystem I (PSI), a key component of the photosynthetic apparatus. These studies suggest the potential photochemical and photophysical impact of some NMS on light-harnessing photosynthetic events.

Vibrational spectroscopic methods are also useful to unravel the vibrational modes and/or functional groups of complex chemical species (Farber et al. 2019; Beć et al. 2020). Especially, Fourier transform infrared spectroscopy (FTIR) utilizes the interaction of matter with electromagnetic radiation at the spectral region of 4000–400 cm^{-1} (2500–25,000 nm). Infrared spectroscopy enables excitation of vibrational or vibrational/rotational transitions of molecules involving transitions from rotational and/or vibrational levels in the same ground electronic state (Avran and Meteescu 1972; Stuart et al. 1996) and can be used to study the fundamental vibrations of pigments during their interaction with NMs (Pontes et al. 2019, 2020). In this respect, vibrational spectroscopy is a powerful and accessible optical technique for environmental monitoring; it is a highly accurate, simple method and requires no sample pre-treatment for measurements (Santos et al. 2022). Additionally, recent studies have shown the possibility of developing a fast and accurate discrimination method for changes on molecular vibrational modes of functional groups by its association with machine learning (ML) algorithms (Larios et al. 2020; Oliveira et al. 2021).

5.7 Electrochemical Behavior of Nanomaterials-Pigment Interaction

The use of solar cells offers great advantages because they take advantage of sunlight, which is an inexhaustible resource and available all over the planet. In addition, they are easy to maintain and install and can be installed in places with difficult access. Currently, commercialized solar cells are predominantly based on monocrystalline or polycrystalline silicon crystals that are produced under optimized temperature and pressure conditions using Czochralski's methodology.

Through the photovoltaic effect, solar cells convert sunlight into electrical energy. Dye-sensitized solar cells (DSSCs) are a promising replacement for traditional silicon solar cells (Fig. 5.8). DSSCs are photoelectrochemical cells belonging to the group of hybrid solar cells as they are formed by organic and inorganic materials. A DSSC has a counter electrode and a photoelectrode, which are often deposited on a glass substrate containing a transparent conductive oxide, such as indium-doped tin oxide or fluorine-doped tin oxide. A mesoporous semiconductor layer, usually TiO_2, is deposited on the conductive surface. In the photoanode, dye molecules for sensitization are attached to TiO_2, and photoexcitation occurs when the dye absorbs light; the dye is oxidized and electrons are injected into the TiO_2 conduction band. An electrolyte with a redox couple ($I^-/I3^-$) is responsible for restoring the original state of the dye. The circuit ends with the migration of electrons through an external
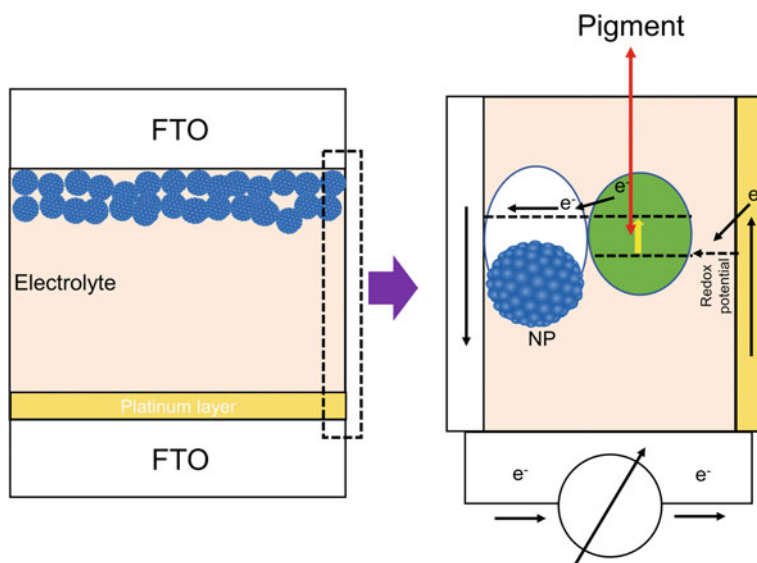
Fig. 5.8 Working principles of DSSC a third generation of solar cell. This type of solar cell was inspired by the photosynthesis process to trap the solar energy that is called as a photon and convert it into electrical energy. FTO: fluorine doped tin oxide electrode; and e$^-$: electron (Figure constructed by the authors)

charge. DSSCs are attractive and promising because they are mechanically resistant, made of relatively low-cost material, and are very easy to process compared with the silicon solar cells that are currently marketed. They can also have their application expanded because they are lighter and can be produced on flexible substrates (Shalini et al. 2015; Orona-Navar et al. 2021).

As sensitizers for third-generation photovoltaic cells, metal complexes, synthetic or natural dyes are used (Zanan et al. 2016; Orona-Navar et al. 2020). Sensitizers based on metallic and organic dyes, such as ruthenium, achieve good photoconversion efficiency (~11%). However, they have disadvantages related to high toxicity, limited presence in nature, exhaustive processes of synthesis and purification, and high cost (Orona-Navar et al. 2020). An interesting alternative for replacing sensitizers based on synthetic dyes and metal complexes are natural pigments such as chlorophylls, carotenoids, anthocyanins, betalains, tannin flavonoids, and phycocyanin (Ranjitha et al. 2020).

These pigments can be obtained from leaves, fruits, and flowers; recently, pigments from microalgae, fungi, and bacteria have also been studied. The main advantages of applying natural dyes as solar cell sensitizers are their low production costs, simple extraction methods, large-scale production, easy handling, and low to minimal toxicity (Orona-Navar et al. 2020).

Among natural pigments, Chls are naturally suitable for efficient light harvesting. However, their application in photovoltaic cells has a strong limitation: high

photodegradation. This is unfortunate because Chls are nature's best photorecep-tors. Thus, if the photostability of Chls could be improved, their technological appli-cation, especially in photovoltaic cells, would be promising because the long-term stability of the molecules is an indispensable prerequisite for this purpose (Barazz-zouk et al. 2012). Therefore, combinations of different natural pigments have shown positive results in DSSC sensitization when compared with the use of individual natural pigments. An example of this is the combination of Chls and carotenoids, where Chls fulfill the light-gathering function and carotenoids act as photoprotec-tors, promoting an improvement in photostability. Furthermore, mixed pigments have also been shown to increase photoconversion efficiency compared with single natural pigments as in the case of the association of Chls and anthocyanins that provide the effect of capturing light in a wider range of the electromagnetic spectrum (Park et al. 2014). However, the photostability of Chls is increased by carotenoids to some extent. Studies show that carotenoids do not protect Chls in vitro as effectively as they photoprotect Chls in vivo. Thus, it is highly imperative to look for an agent that provides efficient in vitro photoprotection of Chls to industrially and biotechnolog-ically enable the use of Chls and other biomolecules as sensitizers for photovoltaic cells (Orona-Navar et al. 2020).

Gold NPs (AuNPs) are described as photoprotective of Chl-*a*, meaning that the photodegradation of Chl-*a* is delayed in the presence of AuNPs. For instance, Barazz-zouk et al. (2012) have shown that AuNPs cause an increase of up to an order of magnitude in the half-life of Chl-*a*. AuNPs can efficiently bind to the nitrogen sites of Chl, resulting in enhanced protection of these pigments (Mezacasa et al. 2020) and, thus, inhibiting the reaction of reactive oxygen species with Chl-*a*, known to cause its degradation under light. Therefore, under in vitro conditions, AuNPs are much better Chl-*a* photoprotective agents than *β*-carotene or quinones (Barazzouk et al. 2012). In addition to the photoprotective capacity of Chls, some NPs when incorporated into the photoanode tend to increase the dye's ability to capture photons from sunlight. Among these materials are metallic NPs, such as silver (AgNPs) or AuNPs, among other metals, which, when incorporated into the TiO_2 structure of the photoanode, improve photon absorption. NPs of noble materials added to a photoanode exhibit surface plasmonic resonance within the device, which is the effect of electron oscil-lation in a structure stimulated by incident light. The solar cell can have embedded Au or Ag NPs to induce the effect, which causes greater absorption and scattering of light and, ultimately, the potential improvement in solar cell performance (Bhogaita and Devaprakasam 2021).

Gold NPs have received special attention due to their electronic and optical prop-erties based on the existence of surface plasmonic resonance. Electrochemical inves-tigations demonstrate that AuNPs on a nanotemplate structure act as an electrical relay (Barazzouk and Hotchandani 2004). Gold NPs are widely used to produce functional electrical coatings; these NMs contribute to improving the redox activity in electrochemical and photochemical applications by easily interacting with organic molecules as in the case of dyes based on biomolecules (Mezacasa et al. 2020). Furthermore, AuNPs can provide better performance in photovoltaic cells due to

their potential to accept and transport the photogenerated electrons in Chl-*a* to the collector electrode (Barazzouk and Hotchandani 2004).

5.8 Computer Aided Simulation for Understanding Nanomaterials-Pigment Interaction

The computational method must be chosen according to your goals, i.e., getting the properties of atomic and molecular bindings, such as intra- and intermolecular energies or conformational positions adopted by NP-pigments, for example. It is certainly important to approach your system before any modeling is begun because computational methods are frequently limited to the number of atoms and/or level of complexity of the studied system. Actually, the available processing power is frequently limited, but not the method specifically. This is commonly known as "computational cost," *i.e.*, the number of required processors to calculate the target variables. From this point of view, a simple exercise of imagination can realize the challenge associated with NPs systems modeling for many atoms.

To optimize the simulation study, the choice of ideal method is important because it has resolution dependence; for instance, calculations can be achieved just to evaluate the disposition and conformation of a pigment on the nanomaterial surface by classical methods or details for atom–atom interactions, including chemical reactions, can be computed from quantum approaches. Nevertheless, it is common to merge the classical and quantum methods in a Quantum Mechanics/Molecular Mechanics (QM/MM) model or to perform two different simulation methods separately. For instance, the best conformation adopted for a target macromolecule (NPs or proteins) with the ligand (pigments) is initially computed by a classical method followed by a quantum calculus to reach some electronic property locally.

There are some important computational methods available to study the interactions of NMs with molecules as detailed by A.S. Barnard for inorganic NPs (Barnard 2010). The in silico methods can be separated basically into two categories: empirical and physics methods (Raunio et al. 2015) as shown in Fig. 5.9. Two important empirical methods are the nano-QSAR and Docking. These methods frequently have an intrinsic theoretical background with quantum and/or molecular mechanics incorporated into them (Santiago et al. 2020).

Nano-QSAR is based on a quantitative structure–activity relationship and is applied to predict biological responses, especially toxicity, based upon the physicochemical properties of NMs available in a set of databases (Puzyn et al. 2009). However, to study the interactions at the molecular level, the docking method is a good beginning. In this case, many strategies have been developed to calculate the best poses for the ligand–target as well as to get its score functions, including genetic algorithmic, fragment-based methods, point complementarity, and distance geometry, among others (Taylor et al. 2002). Molecular docking is widely applied to study protein–ligand systems, but some programs and web platforms have been
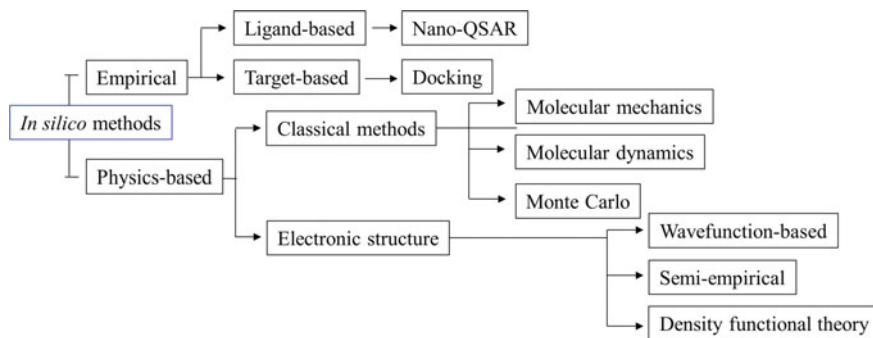
Fig. 5.9 Some computational methods available to study the interactions of pigments and any plant source molecule with macromolecules such as nanoparticles (Figure constructed by the authors)

developed to predict the interactions with the NP surface. An example is the docking calculation performed for the AgNP-xylanase protein (Mishra et al. 2021) using the PatchDock server (Schneidman-Duhovny et al. 2005), a geometry-based molecular docking algorithm program that is a good approach for molecular shape complementarity. Similarly, Fig. 5.10 shows the interaction between the same AgNP of 4.5 nm diameter with *ß*-carotene.

From a predicted conformation adopted by the pigments on the surface of the NMs in the docking calculations, more details for specific interactions in time can be achieved by molecular dynamics. This method is based on the resolution of classical equations of motion; Newton's laws of motion implemented into a numerical
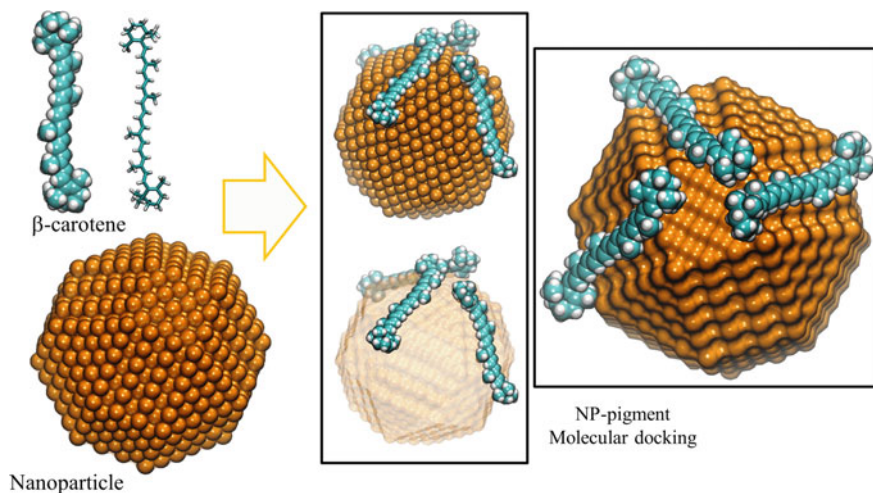
Fig. 5.10 Three conformations were predicted by molecular docking for the AgNP-carotene pigment interaction using PatchDock server for a 4.5 nm diameter sphere (Schneidman-Duhovny et al. 2005). (Figure constructed by the authors)

algorithm, e.g., the Verlet or its variations. Initially, some velocities are attributed to each atom according to the Boltzmann distribution. Then, with a set data of force field parameters for all molecules, the potential interactions are calculated to get the force, which is then used to obtain the acceleration, velocities, and new position coordinates according to a determined time step of integration, commonly one or two picoseconds. These calculations are computed repeatedly to generate a correlated trajectory (Boldon et al. 2015), an advantage in comparison to traditional molecular mechanics or Monte Carlo simulations.

Sometimes, obtaining electronic data for an NP–pigment interaction is desired, such as changes in the response of the radiation interactions and/or electron/energy transfer. For this purpose, an electronic calculation is mandatory. Several methods are available in a set of well-established programs, which are wave function-, semi-empirical-, density functional theory-based, or some derivation thereof (Barnard 2010). These methods are very powerful to investigate interactions at the atom–atom level; however, they are frequently limited to the size of the system due to the high computational cost. Therefore, the quantum approach is applied to a part of the overall system. To illustrate an application of this method, Fig. 5.11 shows an interaction of chlorophyll and pheophytin with gold-NPs performed by our research group (Mezacasa et al. 2020). In this case, to understand the photophysical behavior of these photosynthetic pigments in the presence of Au-NPs, the density functional theory (DFT) was applied. The energies of adsorption were computed as well as the Mulliken charge distribution. The alterations in the absorption and fluorescence profiles of chlorophylls in the presence of the nanomaterial could be associated with the presence of the element magnesium in the structure. The method allows an explanation for the electronic transitions via HOMO–LUMO transfer charges to be suggested.

5.9   Conclusion and Prospects

Current research on the interaction of NMs and plant pigments has opened a new way to view the environmental impact of these materials, and the development of novel technological products. However, ENMs, depending on their dose and physico-chemical properties. may represent a potential risk for plant development and environmental health. The nanomaterial–pigment interaction may change the operation of physiological processes such as the chemical energy production of photosynthesis or flower pollination that involves color-guided pollinators. In this scenario, investigations regarding the interactive effects of NPs on non-foliar plant tissues are still required. Finally, the study of novel nano-enabled materials is essential to assess their potentialities, interaction with the environment, and their effects on other plant organisms; hence, further research on plant pigments is necessary.
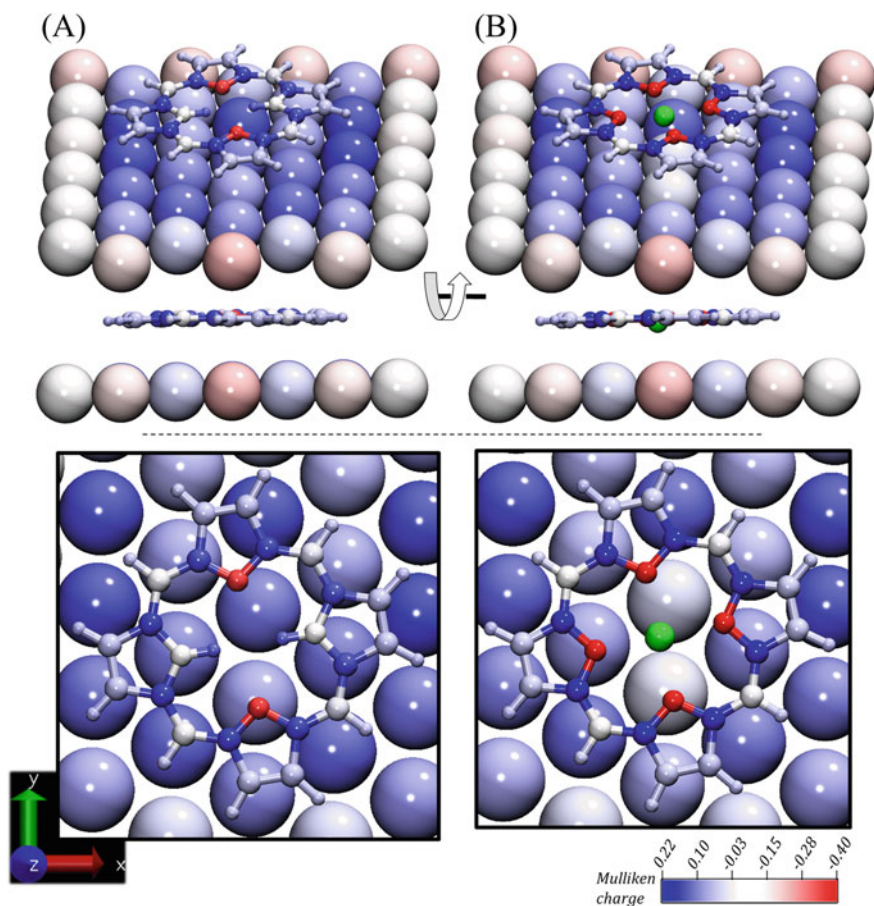
Fig. 5.11 Mulliken charges mapped onto the total electron density of the **A** porphyrin and **B** porphyrin-Mg on gold nanoparticle surfaces. (Figure constructed by the authors)

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